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CONTENTS.

Page

On the Products of the Distillation of Meconic Acid. By John Stenhouse, Ph.D. 1

Further Contributions to the Chemical History of the Products of the Decomposition of Uric Acid. By William Gregory, M.D., F.R.S.E. 9

Additional Observations on Æthogen. By W. H. Balmain, Esq. ... 15

On the Solubility of the Metals in Persulphate and Perchloride of Iron. By Mr. James Napier 16

Observations on Fermentation. By John N. Furze, Esq. 21

Note on a paper on Ferric Acid, read May 16, 1843. By John Denham Smith, Esq. 25

Observations on the Circular Polarization of Light by transmission through Fluids. By H. B. Leeson, M.D., A.M. 26

Observations on Catechuic Acid. By John Thomas Cooper, Esq. ... 45

On a curious Change in the Molecular Structure of Silver. By Robert Warington, Esq. 47

On a Class of Double Sulphates, containing Soda and a Magnesian Oxide. By A. R. Arrott, Esq. 49

Experiments on the Heat disengaged in Combinations. By Thomas Graham, Esq., F.R.S., &c. 51

Note on a Means of Preserving the Crystals of Salts as permanent objects for Microscopic Investigation. By Robert Warington, Esq. 71

Observations on the Green Teas of Commerce. By Robert Warington, Esq. 73

Account of a new Cyanide of Gold. By Mr. John Carty 80

On the Cyanides of the Metals, and their Combinations with Cyanide of Potassium. By Messrs. Charles F. O. Glassford and James Napier :—

Part I. Cyanide of Gold 82

Part II. Cyanide of Silver 92

On the occurrence of Fluorine in Recent as well as in Fossil Bones. By Charles Daubeny, M.D., F.R.S. 97

On a Spathic Carbonate of Iron. By Mr. John Thomas Way 105

Report, &c. 109

On some of the Salts of Meconic and Komenic Acids. By John Stenhouse, Ph.D. 113

Page

On the Reduction of the Salts of Peroxide of Iron by means of Vegetable Substances. By John Stenhouse, Ph.D. 120

On the Hydrate of the Oil of Laurel Turpentine. By John Stenhouse, Ph.D. 121

On East Indian Grass Oil. By J. Stenhouse, Ph.D. 122

Observations on the Pharmaceutical and Chemical Characters of the Peruvian Matico. By John F. Hodges, M.D. 123

On an improved Method for the Detection and Quantitative Determination of Arsenic. By Remigius Fresenius, M.D..... 129

On Fluorine in Recent and Fossil Bones, and the sources from whence it is derived. By J. Middleton, Esq. 134

On the occurrence of Mannite in the *Laminaria saccharina* and other Sea-weeds. By John Stenhouse, Ph.D..... 136

On the Composition of some varieties of South American Guano; with the description of a new mode of estimating Ammonia, and of a process for separating Lime from Magnesia, when these earths exist in combination with Phosphoric Acid. By J. Denham Smith, Esq..... 140

Observations upon the Decomposition of the Double Cyanides by an Electric Current. By Mr. James Napier 158

Abstract of a Letter from H. B. Leeson, M.D., on the Preparation of Fluoride of Iodine 162

On the Composition of Narcotine, and some of its products of Decomposition by the action of Bichloride of Platinum. By J. Blyth, M.D. 163

On the Inorganic Constituents of Plants. By Drs. H. Will and R. Fresenius 179

Examination of a Specimen of diseased Wheat. By Mr. J. Carty ... 199

Analysis of the Bonnington Water, near Leith, Scotland. By Edward G. Schweitzer, Esq. 201

Description of a Chemical Lamp-Furnace. By Edward Solly, Esq. 218

Notice of a new Hydrated Phosphate of Lime. By John Percy, M.D. 222

On a curious Change in the Composition of Bones taken from the Guano. By Robert Warington, Esq. 223

On a means of detecting Kinic Acid. By John Stenhouse, Ph.D. ... 226

Remarks upon Chloranil. By Augustus William Hofmann, Ph.D.... 227

On the Decomposition of Oxides and Salts by Chlorine. By Alexander W. Williamson, Esq. 234

On some of the Substances which reduce Oxide of Silver and precipitate it on Glass in the form of a Metallic Mirror. By John Stenhouse, Ph.D. 242

On the Decomposition of Salts of Ammonia at ordinary Temperatures. By H. Bence Jones, M.D. 244

On some commercial Specimens of Green Glass. By Robert Warington, Esq. 247

On certain Processes in which Aniline is formed. By Drs. J. S. Muspratt and A. W. Hofmann 249

Page

Observations on the Decomposition of Metallic Salts by an Electric Current. By Mr. James Napier 255

On the Distilled Waters of our Pharmacopœias. By Robert Warington, Esq. 261

On the Metamorphoses of Indigo. Production of Organic Bases which contain Chlorine and Bromine. By Dr. August Wilhelm Hofmann, Assistant in the Giessen Laboratory 266

On the Structure of Electro-precipitated Metals. By Warren De la Rue, Esq. 300

On the true Composition of Chlorindatmit. By August Wilhelm Hofmann, Ph.D. 306

Analyses of Farm-Yard Manure, and of Coal-Gas. By Thomas Richardson, Esq. 309

On a New Phosphate of Magnesia. By Wm. Gregory, M.D. 310

Contributions to Actino-Chemistry. By Robert Hunt, Esq., Secretary to the Royal Cornwall Polytechnic Society, &c. 311

On Brown Iron Ore. By Lieut.-Col. P. I. Yorke. 321

Observations on the Action of Animal Charcoal. By Robert Warington, Esq. 326

Annual Report of the Council 329

On Styrole, and some of the products of its decomposition. By Dr. John Blyth and Dr. August Wilhelm Hofmann 334

Note on the useful applications of the Refuse-Lime of Gas-works. By Thomas Graham, Esq., F.R.S. 358

Contributions to the Knowledge of Conjugate Compounds. By Dr. H. Kolbe, Chemical Assistant in the University of Marburg 360

On Toluidine, a new Organic Base. By James Sheridan Muspratt, Ph.D., and Augustus William Hofmann, Ph.D. 367

On the Conversion of Cane-sugar into a substance isomeric with Cellulose and Inulin. By Thomas Tilley, Esq., Ph.D., and Douglas Maclagan, M.D., F.R.S., Edin. 384

On the Action of Bleaching Powder on the Salts of Copper and Lead. By Walter Crum, Esq., F.R.S. 387

Note on the Existence of Phosphoric Acid in the Deep-Well Water of the London Basin. By Thomas Graham, Esq., F.R.S. 392

On a Crystallized Alloy of Zinc, Iron, Lead and Copper. By Warren De la Rue, Esq. 393

Some Experiments on Ozone. By A. W. Williamson, Esq. 395

On the Solubility of Oxide of Lead in Pure Water. By Lieut.-Col. Philip Yorke 399

On Atomic Volume and Specific Gravity. By Lyon Playfair, Esq., Ph.D. and J. P. Joule, Esq. 401

Index 483

Fig: 1.

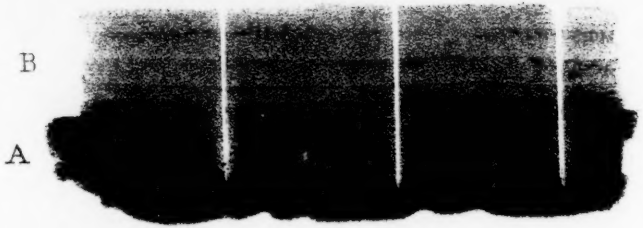
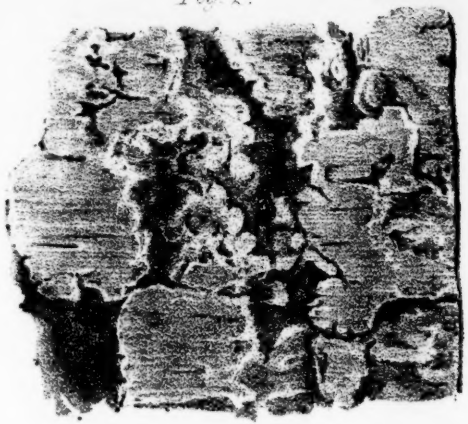


Fig: 2.



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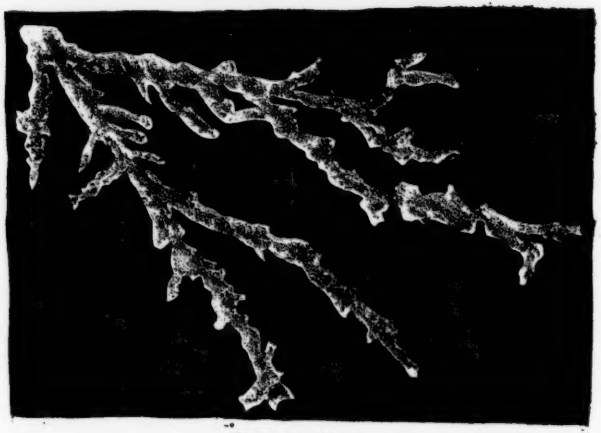
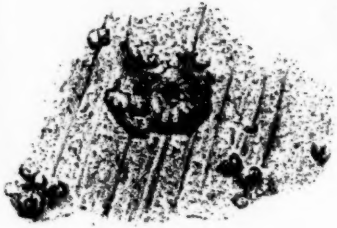


Scale for Fig: 4.
of 1000ths of an inch

Fig: 5.



Scale for Fig. 5
of 2000ths of an inch

Fig: 3.

Scale of Figs. 2 & 3.
of 500ths of an inch

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OF

THE CHEMICAL SOCIETY.

November 7, 1843.—The President in the Chair.

The following books and specimens were presented for the Society's library and museum :—

" Chemical Letters," by Justus Liebig, M.D., Ph.D. Edited by John Gardner, M.D., from the editor.

" Histoire de l'Eau Minérale Sulfureuse d'Allevard (Isère)." " Des eaux, de Source et des Rivières." " Sur la construction et l'emploi du Sulfhydromètre," by Alphonse Dupasquier, Professor of Chemistry in the Medical School of Lyons, from the author.

Papers on various scientific subjects, by Dr. Schœnbein, from the author.

" The London Physiological Journal," No. 1, edited by J. S. Goodfellow, M.D., and Edwin Quekett, Esq., from the editors.

Specimens of the Pyromeconates of Copper and Iron, and of Komenate of Iron, from John Stenhouse, Ph.D.

A specimen of Hyposulphite of Soda in fine crystals, from John Turner, Esq., and one of Chromic Acid, from Robert Warington, Esq.

Theophilus Redwood, Esq. was elected a Member of the Society.

The following communications were then read :—

LXXXV. *On the Products of the Distillation of Meconic Acid.* *By* JOHN STENHOUSE, *Ph.D.*

WHEN either meconic or komenic acids are subjected to distillation at a temperature varying from 510° to 550° F., they yield pyromeconic acid, which passes into the receiver partly as an oily liquid and partly as a crystalline sublimate. Towards the close of the distillation a few crystals of another acid, to which we shall subsequently advert, appear on the sides and neck of the retort.

Pyromeconic acid, as first obtained, is very impure, being contaminated with empyreumatic oil, and some acetic acid; it may be easily freed from the greater portion of these impurities by pressing it between folds of blotting-paper, and cautiously re-distilling it at a comparatively low temperature; the pyromeconic acid is then nearly colourless, and if again pressed and repeatedly crystallized out of spirits of wine, in which it is very soluble, may be easily obtained in large colourless prisms. The acid should be crystallized from rather concentrated solutions and quickly dried, as the crystals become coloured if exposed to the air in a moist state for any length of time. A portion of pyromeconic acid thus purified was dried at 212° F. and analysed in the usual way.

I. 0·381 gramme of substance gave 0·7435 of carbonic acid and 0·123 of water.

II. 0·404 gramme gave 0·783 of carbonic acid and 0·128 of water.

III. 0·323 gramme gave 0·629 of carbonic acid and 0·1105 of water.

	I.	II.	III.	At.	Calculated numbers.		Percent.
Carbon	53·95	53·58	53·84	10	Carbon	= 764·350 =	54·046
Hydrogen	3·58	3·52	3·80	4	Hydrogen	= 49·918 =	3·530
Oxygen	42·47	42·90	42·36	6	Oxygen	= 600·000 =	42·424
	100·00	100·00	100·00			1414·268	100·000

These analyses give the formula $C_{10}H_3O_5 + HO$ for the hydrated acid, which agrees precisely with Robiquet's determination.

Pyromeconic acid, when pure, hardly, if at all, reddens litmus paper, and if a single drop of any of the alkalies is added to its solution, it is immediately rendered alkaline.

In this, as well as in some other respects, it very closely resembles pyrogallic acid, except that pyromeconic acid is not so easily oxidable as pyrogallic acid.

A considerable quantity of an alcoholic solution of potash was added to a portion of pyromeconic acid, also dissolved in hot spirits of wine. The liquid became slightly yellow, and on cooling deposited crystals of the acid containing only a very little potash. The crystals were pressed between folds of blotting-paper and re-dissolved, and on crystallizing them a second time they contained merely a trace of potash, and that obviously owing to the extreme solubility of both the acid and the potash, which rendered their complete separation a matter of some difficulty. A great excess of ammonia was next added to an alcoholic solution of pyromeconic acid, which also soon rendered it slightly yellow. It was dried under the air-pump. The pyromeconic acid crystallized out, with its properties apparently unaltered. It gave no indication of

containing ammonia when boiled with either hydrate of lime or potash. When subjected to analysis—

0·3498 gramme of substance gave 0·6745 of carbonic acid and 0·11 of water.

	Pyromeconic acid.	Calculated numbers.
Carbon . .	53·31	54·046
Hydrogen .	3·49	3·530
Oxygen . .	43·20	42·424
	100·00	100·000

It is obvious, from a comparison of the result of this analysis with the calculated numbers of pyromeconic acid, that the ammonia had not combined with the acid, which, if altered at all, had only been slightly oxidated.

The only salt of pyromeconic acid of which any account has hitherto been published, is the lead salt. It was formed by Robiquet by adding hydrated oxide of lead to a hot solution of pyromeconic acid. When the acid was nearly saturated, the lead compound precipitated; Robiquet found the salt to be anhydrous, and to consist of $C_{10}\ H_3\ O_5 + PbO$.

Pyromeconate of Copper.

When an excess of hydrated oxide of copper is boiled for a short time with pyromeconic acid, the solution becomes of a bright green colour, and when filtered an emerald-green coloured salt is deposited on cooling. It crystallizes in long slender delicate needles, which are very brittle. The crystals require a good deal of hot water to dissolve them, and are very slightly soluble in cold water, or alcohol in either hot or cold. When dried under the air-pump, and then kept for some time at 212° F., they lost no weight. They were subjected to analysis in the usual way.

I. 0·5203 gramme of this salt gave 0·7933 of carbonic acid and 0·1011 grm. of water.

II. 0·3684 gramme gave 0·5633 of carbonic acid and 0·0755 of water.

			Per cent.
I.	0·7292 grm. of the salt gave	0·2002 oxide of copper	= 27·45.
II.	0·3392	0·0917	= 27·43.
III.	1·0113	0·0277	= 27·34.

	I.	II.		Calculated numbers.	Per cent.
Carbon	42·15	42·28	Carbon	10 = 764·350 =	42·522
Hydrogen	2·15	2·27	Hydrogen	3 = 37·438 =	2·099
Oxygen	28·30	28·05	Oxygen	5 = 500·000 =	27·822
CuO	27·40	27·40	CuO	= 495·70 =	27·577
	100·00	100·09		1797·488 =	100·000

This gives the formula $C_{10}\ H_3\ O_5 + CuO$ for the constitu-

tion of the salt, and the number 1301·78 for the atomic weight of the acid, the calculated number being 1302.

Pyromeconate of Iron.

When pyromeconic acid is boiled with hydrated peroxide of iron, it combines with the oxide, and forms a brownish-red powder, which, when neutral, is very little soluble either in hot or cold water. When a few drops of an acid are added, however, it dissolves with a fine deep red colour, and is deposited on cooling in small cinnabar-red crystals. The best way of obtaining this salt in crystals of considerable size and beauty, is by adding persulphate of iron to a tolerably dilute boiling solution of pyromeconic acid, and allowing it to cool very slowly.

The crystals after some hours are deposited in very distinct rhomboids, having a blood-red colour, and a lustre very much resembling garnets. Though not large their crystalline form is easily discernible by the naked eye. The crystals are hard and brittle, and their powder is of a cinnabar-red colour. They are very difficultly soluble either in hot or cold water; and their solutions are of a reddish-yellow colour.

When dried at 212° F. they were subjected to an analysis in the usual way.

I. Determination of the iron: 0·5527 grm. of the salt gave 0·112 of oxide of iron = 19·80 per cent.

II. 0·9135 grm. of the salt gave 0·184 of oxide of iron = 20·14 per cent.

III. 0·426 grm. of the salt gave 0·086 grm. of oxide of iron = 20·19 per cent.

I. 0·421 grm. of the salt, dried at 212° F. and burned with chromate of lead, gave 0·717 of carbonic acid and 0·092 of water.

	Calculated numbers.	Per cent.	Found.
Carbon	30 = 2293·05	46·95	46·80
Hydrogen	9 = 112·315	2·30	2·43
Oxygen	15 = 1500·000	30·71	30·71
Fe_2O_3	= 978·426	20·04	20·06
	4883·791	100·00	100·00

It is evident from these analyses that the iron salt is neutral, the atoms of acid being as three to two. It gives precisely the same formula, $C_{10}H_3O_5$, for anhydrous pyromeconic acid as the lead and copper salts; the atomic weight found being 1299·7; the calculated, 1302.

When oxide of silver is added to a cold solution of pyromeconate of silver, it immediately combines with the acid and forms a bulky light-grayish compound, which is but slightly soluble, and has very little permanence. It quickly decom-

poses even in the cold, becoming of a deep black colour. If it is boiled in a glass tube the inner surface of the tube becomes coated with a mirror of metallic silver, as the oxide is reduced without the evolution of any gas. This reaction with oxide of silver, together with the red colour which the acid strikes with a persalt of iron, form a very easy means of detecting pyromeconic acid.

When pyromeconic acid is added to a solution of nitrate of silver no precipitate or change of colour appears, and it requires to be boiled for some time before even a very partial reduction of the oxide is effected. But if a few drops of ammonia are first added to the nitrate of silver, the pyromeconic acid immediately produces a bright yellow gelatinous precipitate. This precipitate is pretty soluble both in cold water and in alcohol, it also quickly changes its colour even *in vacuo*, becoming dark brown, owing, I apprehend, to partial decomposition. When strongly heated it deflagrates slightly; one portion gave 51·80 per cent. of oxide of silver, which approaches the calculated quantity in neutral pyromeconate of silver, which is 52·70 per cent. of oxide. The examination of this salt is attended with considerable difficulty, owing to its little permanence. Pyromeconic acid occasions no precipitate in solutions of salts of lime, barytes, or strontian. If hydrate of lime however is heated in a solution of pyromeconic acid it dissolves, and when the liquor begins to cool the lime-salt is deposited in small hard crystals, the form of which I was unable to determine.

As Liebig has observed, pyromeconic and pyromucic acids are isomeric bodies; their composition in 100 parts and their atomic weights being the same. They are not identical substances, however, and may be easily distinguished, among others, by the following particulars:—Pyromeconic acid gives a fine red with persalts of iron, while pyromucic acid gives only a dirty green colour; pyromeconic acid does not precipitate basic acetate of lead, while pyromucic acid does so; pyromucic acid reduces oxide of silver, with evolution of gas, as a black powder, while pyromeconic acid precipitates it as a metallic mirror; lastly, pyromucic acid, when boiled with alcohol and sulphuric acid, forms an æther, this pyromeconic acid fails to do. I may mention also, that I was unable to obtain an æther with either meconic or komenic acids.

Pyromeconic acid may be procured in considerable quantity by distilling the acid meconate of copper. This salt falls as a greenish-yellow precipitate when pyromeconic acid is added to acetate of copper. Pyromeconic acid may also be obtained, but in very small quantity, by the distillation of the

neutral meconate of copper. This salt has a fine emerald-green colour, and is formed when a soluble salt of copper is treated with meconate of potash. When meconate of lime is distilled it only yields empyreumatic products, without any trace of pyromeconic acid.

It has already been mentioned that meconic and komenic acids, when distilled, yield small quantities of another acid beside the pyromeconic. Towards the end of the distillation, when the greater portion of the pyromeconic acid has passed over, a few feathery crystals of this second acid condense on the sides and neck of the retort. This acid was first noticed by Gruner and Robiquet. Berzelius has called it the pyrokomenic acid. This name would be very appropriate if this acid were produced by the distillation of komenic acid alone, but it appears not quite so suitable when we consider that the fixed products of meconic and komenic acids are precisely the same. Dr. Gregory considers this acid to be the komenic acid perhaps regenerated. The best way of procuring it is by sublimation, but even this yields it in very small quantity.

A portion of meconic acid was introduced into Dr. Mohr's apparatus, and sublimed at as high a temperature as the paper would bear without charring. The greater portion of the pyromeconic acid, which was also formed at the same time, was either destroyed or dissipated, but a little of it, together with the crystals of the second acid, which I shall call the parakomenic, were found in the cap and on the diaphragm. The crystals of parakomenic acid may be easily separated from the pyromeconic acid, with which they are mixed, by washing them either with cold water or alcohol, in both of which parakomenic acid is but slightly soluble, while pyromeconic acid very readily dissolves.

The parakomenic acid when first sublimed is usually of a deep yellow colour, but this is removed by dissolving it in boiling water, and digesting it with animal charcoal. When the filtered solution cools, the parakomenic acid is deposited in hard crystalline grains, with merely a faint tinge of yellow; their powder is quite white. The crystals of parakomenic acid, if not quickly dried, become of a pale red colour, and their solutions, though reddish while cold, become nearly colourless when heated. In appearance, degree of solubility in water and alcohol, and in their strongly acid taste and reaction, they closely resemble komenic acid, from which they differ however in some particulars, as I shall presently notice. When dried at 212° F. and analysed with chromate of lead,—

I. 0·3319 gramme of substance gave 0·5603 grm. of carbonic acid and 0·0805 of water.

II. 0·2788 gramme of substance gave 0·470 of carbonic acid and 0·071 of water.

III. 0·3873 gramme of substance gave 0·653 of carbonic acid and 0·0912 of water.

	I.	II.	III.	At.		Calculated numbers.
Carbon	46·67	46·61	46·62	12	Carbon	46·62
Hydrogen	2·69	2·82	2·61	4	Hydrogen	2·53
Oxygen	50·64	50·57	50·77	10	Oxygen	50·85
	100·00	100·00	100·00			100·00

It is evident from the results of these analyses, that the composition per cent. and formula, both of komenic and parakomenic acids, are the same. Though this is the case, and though they closely resemble each other in most of their properties, the two acids may be easily distinguished by the following reactions:—I. Parakomenic acid produces no precipitate in a solution of acetate of copper, while komenic acid causes a copious yellowish-green precipitate. II. When added to neutral acetate of lead, parakomenic acid throws down a small quantity of a white granular precipitate, which instantly disappears if the liquor is stirred, being apparently dissolved by the free acetic acid present, for it reappearsa nd remains permanently on the addition of a few drops of ammonia. Komenic acid, on the contrary, causes in acetate of lead a bulky, slightly yellowish precipitate, which does not dissolve even when treated with a great excess of acetic acid. Neither komenic nor parakomenic acids precipitate salts of lime, barytes, or strontian. They produce no change in solutions of corrosive sublimate or chloride of platinum. They agree in giving a pale red to a solution of tartar-emetic, but cause no precipitate. Parakomenic acid also closely resembles komenic acid in its silver salts, of which it appears to form two. When a solution of the acid is added to nitrate of silver it occasions a copious white granular precipitate, and when the acid has been previously neutralized with ammonia it gives with nitrate of silver a yellow gelatinous precipitate. I attempted to determine the atomic weight of parakomenic acid from a small quantity of these salts, but the results were unsatisfactory, and unfortunately I have not yet been able to procure enough of the acid to enable me to repeat them.

I may mention however that both salts gave less of silver in the 100 parts than the corresponding salts of komenic acid. Both acids also give a similar deep red colour with persalts of iron, and on standing for a few hours they both yield a quantity of small, hard, jet-black crystals, of which, in the instance of komenic acid, a description and analysis is

herewith subjoined. The crystals formed by parakomenic acid cannot be distinguished by their appearance and general properties from those of komenate of iron, though the composition is probably different.

Komenate of Peroxide of Iron.

When persulphate of iron is added to a cold and pretty concentrated solution of komenic acid, the liquid becomes of a deep blood-red colour. After standing for some hours it grows paler, and a considerable quantity of very small jet-black crystals are slowly deposited on the sides and bottom of the vessel. These crystals have a considerable resemblance to coarsely-pounded charcoal, but they possess a much higher lustre. In chemical authors komenic acid is said to form a very soluble salt with peroxide of iron. This is a mistake, however, and can only have arisen from the circumstance that this black powder is so unlike a salt, that it has hitherto been overlooked. The crystals are very hard, are gritty between the teeth, and have scarcely any taste. They are difficultly soluble in either cold or hot water. When rapidly washed with cold water it runs off nearly colourless, but if the water is kept for some time standing over them, it becomes of a pink colour. Their solution in boiling water has a pale red colour. Their powder is dark reddish-brown. They were dried at 212° F. and subjected to analysis.

				Percent.
I.	0·4230 gramme	gave 0·0784	peroxide of iron	= 18·53
II.	0·4696 ...	... 0·086	... ...	= 18·31
III.	0·4325 ...	... 0·081	... ...	= 18·72
IV.	0·3434 ...	... 0·0645	... ...	= 18·76

I. 0·3534 gramme, when ignited with chromate of lead, gave 0·450 carbonic acid and 0·0953 water.

II. 0·3510 gramme gave 0·444 of carbonic acid and 0·0920 of water.

	I.	II.	At.	Calculated numbers.	Percent.
Carbon	35·20	34·97	24	Carbon = 1834·440 =	34·94
Hydrogen	2·99	2·84	11	Hydrogen = 137·274 =	2·61
Oxygen	43·23	43·61	23	Oxygen = 2300·000 =	43·80
$Fe^2 O^3$	18·58	18·58		$Fe^2 O^3$ = 978·424 =	18·63
	100·00	100·00		5250·138	100·00

These analyses give the formula $KO + 2\,HO + KO + HO + Fe_2 O_3 + 4\,aq = C_{12} H_4 O_{10} + 2\,HO\,C_{12} H_4 O_{10} + HO + Fe_2 O_3 + 4\,aq$.

The salt employed for these determinations was made at three different times.

Komenate of ammonia, when treated with persulphate of

iron, also yields this salt, just as when the acid alone is employed. I determined the quantity of iron contained in a portion of salt made in this way and dried at 212° F. 0·2782 gramme gave 0·052 of peroxide = 18·69 per cent.

If persulphate of iron is added to a hot instead of a cold solution of komenic acid, which is kept for some hours at a temperature of about 150° F., none of these jet-black crystals are deposited. The red colour also of the liquid disappears, and it becomes transparent, and has a deep yellow colour.

A solution of galls produces in it no change of colour, but it gives a deep blue with red prussiate of potash, and a white precipitate changing to blue with the yellow prussiate. These reactions clearly show that the peroxide of iron has been reduced by the komenic acid to the state of protoxide. The red colour of the liquid was not restored by the addition of more komenic acid, but it immediately returned when more persulphate of iron, or a little nitric acid was added A considerable quantity of persulphate was poured into the liquid, which was then set aside in a hot stove for twelve hours, when its red colour had again disappeared, and a small quantity of bright yellow crystals were found at the bottom of the liquid. These crystals were but of small size, but larger than those of the komenate of iron; they possessed considerable lustre, and were but slightly soluble in cold water. When heated they inflamed and left a considerable quantity of black oxide of iron, which showed that they consisted of an organic protosalt of iron.

If the crystals are digested with solution of potash the iron is precipitated in the state of protoxide; and when the clear alkaline liquor is separated and is neutralized with muriatic acid, it does not strike a red colour with persulphate of iron, which clearly shows that the acid in these crystals is not the komenic.

LXXXVI. *Further Contributions to the Chemical History of the Products of the Decomposition of Uric Acid.* By William Gregory, *M.D., F.R.S.E.*

IN 1840 I described, at the Glasgow Meeting of the British Association, an improved and very productive method of preparing alloxan, murexide, &c.; and I showed, from the occurrence of urea among the products of the action of hypermanganate of potash on uric acid, that Liebig and Wöhler's view, according to which urea pre-exists in uric acid, must be admitted, in the present state of our knowledge, as well-

founded; thus giving additional probability to the supposition of the existence of the acid supposed by them to be present in uric acid, combined with urea, and called, hypothetically, urilic acid = $C_8 N_2 O_4$.

Since that period I have been frequently occupied with the subject of uric acid. In 1841, Professor Liebig having entrusted to me the treatment of upwards of 2 lbs. of urate of ammonia, I extracted the uric acid from this, and converted nearly the whole of it into alloxan, of which I obtained $1\frac{1}{2}$ lb. in large and absolutely pure crystals. This not only enabled me to study the preparation of several of the other products, but led me to economise as much as possible the very abundant mother-liquid of the alloxan, which contained a large quantity of that substance, but so much mixed with nitrate of ammonia and free nitric acid, that the alloxan could not be purified by crystallization, even if the liquid could have been concentrated by heat without decomposition. I shall now state the results of my experiments, as far as these are tolerably ascertained. There is still much to be done, and several investigations are in an imperfect state in my laboratory. As it may be some time however before I may be able to return to them, I think it right, in the mean time, to describe the results hitherto obtained.

1. *Alloxantine.*

This compound is best obtained from the mother-liquid of alloxan, as prepared according to my process*. The acid solution is diluted with two or three parts of water, and a current of sulphuretted hydrogen gas is passed through as long as it produces any effect. Sulphur is first deposited, and subsequently a large quantity of alloxantine. The mixed precipitate is drained, washed with a little cold water, and then boiled with water, acidulated with hydrochloric acid, until all the alloxantine is dissolved, which requires from a quarter to half an hour, even when enough water is present for the final solution of the whole. The solution is filtered while hot, which takes place very rapidly, and deposits on cooling an abundant crop of crystals of alloxantine. The quantity reaches its maximum in twenty-four hours, and the amount retained in the acidulous mother-liquor is but small. It may however be obtained by concentration. By this method the mother-liquid of the alloxan above mentioned, although some part of it was used for other experiments, yielded upwards of 8 oz. of pure alloxantine.

* See Turner's Chemistry, 7th edition.

2. *Dialurate of Ammonia.*

This salt may be also obtained in abundance from the mother-liquid of alloxan, as well as from that of alloxantine. Ammonia is to be cautiously added in the cold, so as to leave a slight excess of acid, and hydrosulphuret of ammonia is to be then added in excess, so as to redissolve any sulphur that may be at first thrown down. The dialurate is formed in the cold so abundantly as to cause the whole to become thick. It may be dissolved in the liquid by the aid of heat, and it is then deposited on cooling in crystals. We ought to see that nothing is left undissolved by the hot liquid; should this occur it is probably owing to sulphur, and in that case a little hydrosulphuret of ammonia clears all up. The crystallized dialurate of ammonia is collected on a filter and washed, at first with a weak solution of hydrosulphuret of ammonia, then with alcohol, to which enough hydrosulphuret has been added to give it a pale yellow colour, and finally with pure alcohol till the latter passes through quite colourless and pure. The salt is quickly submitted, while still on the filter, to pressure between folds of bibulous paper, and is finally dried *in vacuo* over sulphuric acid. Should it not appear pure, the process of dissolving it in water with the addition of hydrosulphuret of ammonia, of crystallizing, and washing as above, is to be repeated. By this method I have prepared this salt in large quantity, and have obtained it dry and quite pure, with only a faint tinge of flesh colour, in fact almost colourless. If dried in the air, without the use of the alcohol and hydrosulphuret in washing, and with the aid even of a gentle heat, it becomes blood-red.

The pure dialurate forms minute prismatic crystals, which are united together when dried in light bulky masses of a faint silky lustre. I took advantage of the possession of a large stock of this salt to repeat the analysis of it, determining the nitrogen by the process of Varrentrapp and Will. Several analyses made by myself, and one made by Mr. Keller, yielded results which I shall not detain the Society by repeating, as they agreed entirely with those of Liebig and Wöhler.

3. *Dialuric Acid.*

Liebig and Wöhler failed to obtain this acid in a separate form, owing doubtless to their being compelled to make their experiments on very small quantities. I found that it is easily obtained when the preceding salt is dissolved, with the aid of heat, in an excess of diluted hydrochloric acid. The liquid deposits on cooling a quantity of sparingly soluble crystals,

not unlike those of alloxantine, yet quite distinguishable from them; these crystals are dialuric acid. They have a strong acid reaction, and readily neutralize the alkaline bases, forming, with ammonia, the preceding salt; with potash, a sparingly soluble salt in hard crystals; and with baryta an insoluble or very slightly soluble powder. The latter salts are formed when dialuric acid is added to solutions of the soluble salts of potash and baryta, so that the affinities of the acid are powerful.

Dialuric acid is not however very permanent in its uncombined form, that is to say, when dissolved in water. It gradually passes into alloxantine when exposed to the air, oxygen, no doubt, being absorbed. The change may be traced in the colour of the precipitate produced by barytic water. If it be white, the acid has not yet undergone a change; but if it be pale pink, reddish-purple, or violet, this indicates the gradually increasing proportion of alloxantine. Even the crystals of dialuric acid, when left in the liquid from which they have been deposited for a day or two, are found to be partially changed into alloxantine.

I made several analyses, both of the acid itself and of its compounds, with potash and baryta. The details shall appear hereafter: at present I may state that these analyses correspond to the hypothetical formula given by Liebig and Wöhler, namely $C_8\ N_2\ H_4\ O_8 = C_8\ N_2\ H_3\ O_7 + HO$, in which HO seems to be capable of replacement by MO in the salts. It is important to observe that urile or urilic acid, $C_8\ N_2\ O_4 + H_4\ O_4$, = 4 atoms of water, contains the elements of dialuric acid.

It is proper to state that Liebig and Wöhler did obtain by the same process as I adopted the crystals of dialuric acid, which, however, appear to have been partially converted into alloxantine before they were examined*. Indeed my experiments lead me to believe that the substance described by these chemists as dimorphous alloxantine is nothing but dialuric acid, more or less completely converted into alloxantine, and retaining probably its original form. Or they may have examined a mixture of the crystals of both, in which those of dialuric acid happened to be the largest and best formed. Such a mixture, if analysed, would of course yield results closely approximating to those derived from alloxantine, as the latter body consists of the same elements as dialuric acid + 1 at. of hydrogen and 2 at. of oxygen only. Liebig and Wöhler have already observed, and my experiments confirm the statement, that the liquid obtained by boiling dialurate of ammonia with an acid, deposits, when allowed to stand for

* *Ann. der Pharm.*, xxvi. 280.

some time after cooling, crystals of alloxantine, which will of course be found mixed with the dialuric acid deposited during refrigeration, unless the latter be first separated.

The salts of dialuric acid in the dry state are quite permanent. I am still occupied with the study of this remarkable acid and its salts.

4. *Acid Thionurate of Ammonia.*

This salt, from which, according to Liebig and Wöhler, the uramilic acid is best obtained, may be prepared in any quantity by dissolving the neutral thionurate of ammonia in hot water, and adding exactly as much hydrochloric acid, calculated from the specific gravity by means of the published tables of liquid hydrochloric acid, as corresponds to 1 eq. of hydrochloric acid for 1 eq. of the salt, which contains 2 eq. of ammonia. One of these is removed by the hydrochloric acid, and when the liquid is gently evaporated to a small bulk it deposits the acid (monobasic) thionurate of ammonia in soft crusts, which frequently fall to the bottom, and are composed of very minute prisms. I have not yet succeeded in obtaining uramilic acid either from this salt or in any other way; and Prof. Liebig informs me, that neither he nor Prof. Wöhler has been so fortunate as to succeed in procuring it again. It can hardly be doubted, however, that with an easy and sure method of preparing the acid thionurate, we shall soon ascertain all the conditions essential to the formation of uramilic acid. The acid thionurate itself, as well as all the compounds now mentioned, I have prepared by ounces at a time without once failing.

5. *Alloxano-sulphurous Acid.*

Liebig and Wöhler mention that a solution of alloxan in sulphurous acid, when slowly evaporated, deposited large tabular acid crystals, which not only were not thionuric acid (which requires the elements of ammonia besides those of alloxan and sulphurous acid), but, when mixed with ammonia, did not produce the thionurate of that base but a totally different salt, of a gelatinous aspect, which has not been further examined. I have not examined those tabular crystals, nor, indeed, have I as yet seen them; but I have by other means obtained a salt, the acid of which appears to be composed of alloxan and sulphurous acid.

To obtain this salt, dissolve alloxan in the smallest possible quantity of cold water, and add to the solution a slight excess of a saturated solution of sulphurous acid in water. Then add, with care, caustic potash in solution till there is the

slightest possible alkaline reaction. There will be deposited very soon, partly even at once, in the cold solution a salt in hard brilliant crystals, which may easily be obtained, by recrystallization, of considerable size, and are very beautiful, from their perfect whiteness, their transparency and brilliant lustre. This new salt may be procured in any quantity and with the utmost facility. I have not yet succeeded in isolating the acid, but the analysis of the salt indicates that the acid consists of two atoms of sulphurous acid and one of alloxan. It thus differs from thionuric acid by the absence of 1 eq. ammonia, and probably also in being monobasic, while thionuric acid is bibasic. The analytical details concerning this new acid, which I propose to call the alloxano-sulphurous, will appear when I have completed my investigation of its properties. It is probable that the large tabular crystals above mentioned, as obtained by Liebig and Wöhler, are nothing more than the alloxano-sulphurous acid in a free state.

6. *Alloxanic Acid.*

When pure alloxantine is dissolved in distilled water, and the cold solution allowed to stand, it slowly loses the property of giving a violet precipitate with barytic water, and finally yields a white precipitate.

The liquid is now acid, and if gently evaporated to dryness yields crystals, which are very soluble both in water and alcohol, and which possess all the chemical characters of alloxanic acid. Professor Liebig did me the favour to examine these crystals as obtained by me, and considered them to be alloxanic acid, as I had previously done. I did not consider them pure enough for analysis, and besides their analysis could throw little light on the subject, as the crystallized alloxanic acid has the same composition in 100 parts as anhydrous alloxan; and differs, therefore, from alloxantine only by containing 1 eq. of hydrogen less.

Should this observation be confirmed, it seems difficult to account for the production of alloxanic acid in this experiment. No other compound appears to be formed, and the change seems to take place as well in tightly corked and filled vessels as in the air. Besides, when alloxantine is oxidized, it yields, not alloxanic acid but alloxan, and there is no base present that might be supposed to give rise to the production of the acid.

It is possible that this acid may not be really alloxanic acid, although agreeing with it in its reactions. In that case it appears most probable that it may be isomeric with alloxantine, as alloxanic acid is with alloxan. At all events, it is

impossible to see how the 1 eq. of hydrogen has been removed, if the acid be really the alloxanic. I am still engaged in researches on this part of the subject, the results of which I shall forward to the Society at a future period, along with those of the other investigations briefly described above. The study of the products of the decomposition of uric acid is still very far from being completed, and I hope, at no very distant period, to follow up this paper with another on the same subject.

LXXXVII. *Additional Observations on Æthogen.* *By* W. H. Balmain, *Esq.*

ON proceeding to make some quantitative experiments on æthogen, I found, that through depending too much upon simple change of property, I had been misled upon some points; and I take this, the earliest, opportunity of pointing out in what respects my conclusions were erroneous.

All the compounds described as æthonides are one and the same substance, a new compound of boron and nitrogen, probably formed by the decomposition of the æthonide of the metal by the nitro-muriatic acid used at the end of the process. It would appear that there are two compounds of boron and nitrogen; one, which is not altered by exposure to a white heat, is decomposed by the action of water at ordinary temperatures, and also by the action of nitric acid, and which does not phosphoresce before the blowpipe; and a second, which is not decomposed by any reagents, with the exception of water and oxygen at a high temperature, and which phosphoresces beautifully before the blowpipe. The first is formed when mellon and boracic acid are heated together and combines with the metals; the second whenever a compound of the first with a metal is decomposed by abstraction of the metal, which is effected with such difficulty, that the traces left induced me to suppose that it was an essential element of the compound. Whether or not these two compounds are isomeric, remains yet to be ascertained.

The simplest method of preparing the phosphorescent compound is to heat together 12 parts of cyanide of mercury, $1\frac{1}{2}$ of boracic acid, and 1 of sulphur.

The compound of phosphorus and nitrogen (discovered by Rose) probably has similar relations, and may perhaps be studied to advantage in connexion with the above; an easy method of preparing it is to place some chloro-amidide of mercury in a flask, and add from time to time a portion of phosphorus, keeping up a gentle heat all the time, and agi-

tating now and then; and when the phosphorus ceases to produce any decomposition, raise the temperature nearly to redness.

November 20, 1843.—Robert Porrett, Esq., Treasurer, in the Chair.

The following works were presented to the Society:—

"Fresenius on Chemical Analysis," translated and edited by Loyd Bullock, Esq., from the editor.

"A New Method of Alkalimetry," by Drs. Fresenius and Will; translated and edited by Loyd Bullock, Esq., from the editor.

"A Series of Chemical Tables and Labels," by Messrs. Charles Button and Warren de la Rue, from the authors.

"Taylor's Calendar of the Meetings of the Scientific Bodies of London," for 1843 and 1844, from the editor.

The following papers were then read:—

LXXXVIII. *On the Solubility of the Metals in Persulphate and Perchloride of Iron.* By Mr. James Napier.

THE following observations have been lying in an unfinished state for some months past, in hopes that time would allow me to make more investigations into some of the phænomena developed; but owing to urgent duties, altogether apart from such investigations, I have little hopes of being able to fulfil these intentions; I have therefore collected them together, in hopes that it might attract the attention of some one more qualified to give them that investigation which their singularity seems to deserve.

I may be allowed, in the first place, to relate the circumstances which led me to the observations which follow. Hearing of the great quantity of water which is constantly issuing from the Pary's Mines, Anglesea, impregnated with copper, and the great expense of obtaining this copper, I thought it probable that it might be extracted by means of a galvanic current, or what is known as the electrotype process. For the purpose of trying experiments upon this subject, I was kindly favoured with a quantity of the water, with the following details:—Quantity of water issuing from the mines yearly, 700,000,000 gallons; this is collected in pits, into which is put old iron, which precipitates the copper. The average product of copper is from 55 to 60 tons; the iron consumed in obtaining this is 600 tons. The copper found in these waters, as indicated from the precipitate obtained, varies from 4 to 30 per cent., according to the wetness of the season; the sample I procured was during the dry season, and consequently rich in copper; its specific gravity was 1·055 at 60° F. The solid contents of one gallon weighed 4960 grains, which gave

peroxide of iron 1680 grains, oxide of copper 80 grains, sulphuric acid 3040 grains, muriatic acid 38 grains, and 122 grains of earthy matters, which were not examined. The iron existed in the water as the persulphate. My first operation was one I had found to answer in analysing copper ores, namely, wrapping a strip of brown paper round a piece of iron, attaching this to a piece of copper, and immersing them both in the solution of the copper ore, in muriatic acid, to be examined; but I found that the first action which took place was the complete reduction of the persalt of iron to the state of protosalt, at the expense of the copper pole: after which the electric current began to effect its object, the copper being deposited, but from the copper which had been dissolved having also to be deposited, the consumption of iron was 658 grains, while the actual increase in the weight of the copper pole was only 64 grains, the quantity of copper originally held in solution. The reaction which took place may be expressed as follows:—

1680 grains of peroxide of iron composed of	iron	582·7	protosulphate of iron.
	iron	582·7	
	oxygen	171·5	
	oxygen	171·5	
	oxygen	171·5	sulphate of copper.
2568 grains of sulphuric acid.	acid	856·0	
	acid	856·0	
	acid	856·0	
Copper pole.	copper	690·7	

giving 690·7 grs. + 64 grs. to be deposited by the electric current. Different arrangements of batteries were tried; platinum, silver and lead were also substituted for the copper, but in no case was a deposit obtained from the water until the iron was first brought into the state of a protosalt; but when this was effected, I obtained by the method first described 63 grains of copper by the loss of 58 grains of iron.

During these experiments I found that silver, tin, lead, antimony, bismuth, cobalt, nickel, and several other metals were very soluble in neutral persalts of iron, reducing it to the state of a protosalt. In order to repeat these experiments, I prepared some perchloride of iron in the following manner, adding to the boiling solution of the sulphate as much nitric acid as was necessary to peroxidize the iron, then precipitating by ammonia, washing this well with hot water, and dissolving with hydrochloric acid, evaporating nearly to dryness, and adding a quantity of distilled water. The persulphate used was obtained as a dry white powder; both salts were neutral.

I was aware that Professor Fuchs had recommended the

boiling of a piece of clean copper in perchloride of iron as a means of ascertaining the quantity of iron in an ore of that metal, and also to ascertain the amount of copper in certain copper ores. For iron ores I have found great difficulty in obtaining uniform results, from the great difficulty of knowing the exact period at which the iron is all reduced to the proto state, for the copper put in continues to dissolve until the chloride is all converted into a subchloride; this result is effected, however, much more rapidly when the iron salt is neutral than when it contains free acid, a condition specially recommended by Fuchs.

The most uniform results are obtained by allowing the copper to remain until the solution becomes colourless; on diluting with cold water, the whole of the copper is precipitated as a white powder; the clear solution, if the process is completed, will contain no copper, when there will be two equivalents of copper dissolved from the metal for every equivalent of peroxide of iron formerly in the solution. It occasionally happens, however, when neutral salts of iron are used, that the copper becomes encrusted with a white deposit, upon which crystals of the subchloride of copper collect, and thus protect it from further action; this is prevented by boiling, or taking out the copper, removing the crust, washing it, and putting it into the solution again, when the action goes on as before. When the persulphate of iron is used for this purpose instead of perchloride no subsalt is formed, and the result is uniform, one equivalent of copper being dissolved for every equivalent of peroxide of iron present in the solution.

I may mention one especial application of the solubility of copper in perchloride of iron, namely, the dissolving copper from the surface of silver, such as copper that has been used as a mould in which silver has been deposited; when this solution becomes saturated with copper, a little ammonia added precipitates the iron as a peroxide and combines with the copper, forming a soluble double chloride, which may be immediately separated by filtration and the precipitate washed, the peroxide of iron again dissolved in hydrochloric acid is fitted for a renewal of the same operation. I may here mention, that if, previous to adding the ammonia, there be a little perchloride of iron put into the mixture of subchloride of copper and protochloride of iron, an immediate change is effected, the colour of the solution becomes green, and on adding ammonia to this, both copper and iron are precipitated.

Persulphate of iron cannot be used for the purpose of dissolving copper from silver, both from the easy solubility of silver in solutions of this salt, and also from a peculiar de-

structive action which it has upon alloyed silver. Standard silver is completely destroyed. I have used thin sheets, weighing from 60 to 70 grains, and when only 4 grains were apparently dissolved the remainder had been so much affected that it crumbled between the fingers like a dried leaf.

When silver is put into a solution of persulphate of iron an immediate action takes place, a yellowish cloud begins to form in the solution; if heated the action is much more rapid, a yellow oxide of iron forming upon the sides of the vessel, and there is also a brown precipitate deposited; the iron in the solution is converted into the proto state, shining particles of metallic silver float through the solution, and sulphate of silver crystallizes on the vessel, but in no case did I find an equivalent of silver for the equivalent of peroxide of iron; by slow evaporation the solution yielded crystals of protosulphate of iron and sulphate of silver.

Tin is very easily dissolved in both the persulphate and perchloride of iron, completely reducing them to the proto state. When the solution is cold this is effected in about an hour; when hot, in a few minutes; the iron is reduced to the proto state when only half an equivalent of tin is dissolved for every equivalent of peroxide; my first impression was, that the first atoms of protosalt of tin formed reduced a corresponding atom of peroxide of iron, and was converted into a persalt; but saturating with ammonia, and adding it in great excess, the precipitated oxide of tin was not redissolved, and had every other character of a protosalt. Whether this was owing to the formation of *a bisulphate or bichloride of tin*, I did not ascertain; but by boiling or long standing there is an equivalent of tin dissolved for every atom of perchloride of iron, but I did not obtain the same result in the persulphate.

Cadmium is very soluble in persalts of iron; in the persulphate an equivalent of cadmium is dissolved for the equivalent of persulphate of iron; but in perchloride of iron 2 equivalents of cadmium are dissolved for every equivalent of perchloride of iron, forming, as in the case of copper, a subchloride, which was not precipitated by the addition of water.

Lead is also dissolved in persalts of iron, reducing a portion of the iron to the state of a proto salt; the lead becomes covered with a thin crust of sulphate or chloride, which seems to protect it from further action; when the iron solution is boiled with the lead much more is dissolved, and a precipitate of peroxide of iron collects at the bottom. This action of iron on lead may account for the rapid destruction of leaden tanks, noticed by Mr. West at the last Meeting of the British Association, that when spring water, which had been running

into a lead tank for many years without the slightest action upon the lead, was conveyed through iron pipes to the tanks, the tanks were destroyed in six years.

Antimony is not very soluble in persulphate of iron even when heated, but it is very soluble in perchloride of iron when hot, reducing the iron to a protochloride in a short time, the solution becoming of a light brownish colour. I found that if kept boiling slowly for a long time the antimony loses an equivalent of metal for every equivalent of peroxide of iron, giving us the idea of the existence of a compound of antimony with chlorine of one to one. This solution was not examined further than by dilution with water, which precipitated almost all the antimony as a white powder, undergoing the usual changes of common chloride, except when the dried precipitate was boiled in nitric acid, in which it dissolved with the evolution of nitrous gas.

Arsenic is very soluble in perchloride of iron, reducing the iron to the state of protochloride, losing also with long boiling an equivalent of metal for every equivalent of peroxide of iron in the solution; but this result is not obtained without long boiling.

Bismuth is very soluble in perchloride of iron, slightly in persulphate; the perchloride is completely reduced to the state of protochloride, a full equivalent of metal being dissolved for the peroxide of iron present; this is wholly precipitated by dilution.

Cobalt is very soluble in perchloride of iron, reducing it completely, changing the solution to a pink colour; the cobalt salt formed crystallizes from this solution very easily.

Nickel is also soluble in perchloride of iron, giving a precipitate of brown oxide of iron; the solution becomes green, containing protochloride of iron and nickel; a portion of the nickel is precipitated as a fine white powder by dilution.

Platinum in persulphate and perchloride of iron produced no change, neither lost anything in weight.

Gold boiled for a long time in perchloride of iron in two experiments lost 0·2 and 0·3 of a grain. In both these instances beautiful crimson-red crystals, in perfect octahedrons, were obtained, adhering to the metal and also to the containing vessel. I did not try whether they contained any gold. These results were only obtained twice in six different trials; they were procured with iron prepared at different times. Platinum was always tried at the same time with the gold, and when there was no gold dissolved I never obtained any crystals.

I need hardly mention that both zinc and iron, when put

into the persalts of iron, first reduce the persalt to the protosalt, which fully accounts for the great consumption of iron for the small quantity of copper obtained in these waste waters of mines, and not, as was generally supposed, from the existence of free acid; the copper is never all precipitated from the water so long as persalts of iron exist in the solution. The presence of persalts of iron also prevents the deposition of the copper by a galvanic current; the proportionate quantity of persalts of iron necessary to resist completely the deposition of copper was not ascertained.

In no one case did I find any double salt formed between the iron and metal dissolved in it, but when the solution containing them was evaporated the salts of the two metals crystallized separately.

In all cases where the process is conducted cold the solution of the metal takes place at the bottom of the vessel and progresses upwards; this is beautifully exhibited when a tall glass is used with a solution of perchloride of iron, and a slip of copper reaching to the bottom; the solution first becomes green at the lower part, and this advances slowly upwards till it reaches the top, but before the change of colour reaches the top the bottom has become colourless from the formation of subchloride.

I may observe that the whole of these remarks are only the prominent features noted down as they occurred, without any idea of bringing them before the Society in this unfinished state; but having no hope of obtaining leisure for making further investigations, I have given them as they are, thinking that perhaps some one, having more time and ability, would repeat the experiments and produce something more definite.

LXXXIX. *Observations on Fermentation.* *By* John N. Furze, *Esq.*

In consequence of the practical inconveniences arising to brewers from want of control over the fermenting tuns, and the changes in the worts dependent upon atmospheric temperature, I was led to the following experimental observations.

The infusion of malt being made according to the usual practice of brewing, the wort, or infusion, is boiled with the hops, and being subsequently cooled, yeast to the amount of about one pound by weight to the barrel of wort is added, and the whole transferred to the fermenting tun. The general form of a brewer's fermenting tun being that of a simple open vessel,

the worts lie exposed during their change of state without covering and with free access of air. This, as is evident, must expose the fermenting mass to the variations of atmospheric temperature, which, in their turn, either check or hasten the operation to such an extent, that the ultimate success of the brewing is endangered, and not unfrequently considerable loss is sustained. These disadvantages are occasionally avoided in some of the larger breweries by the use of fermenting tuns, which are so far inclosed as to leave but sufficient space for the escape of the gaseous matters arising from the surface of the worts when the fermentation is in full vigour.

Having tried the above method without finding the desired advantage to result from it, new measures of proceeding were taken, as follows:—A circular tun was erected, whose total content was 350 barrels, having a door in the side capable of being made air-tight by lining its edges with coarse serge and applying screw-pressure to the centre of it. To the upper part of this tun, which was fitted with windows in the top and sides to afford to the brewer an opportunity of viewing the apparent changes in the worts, two India-rubber pipes were attached, each of 1 inch internal diameter, to convey away the gas generated during the process; and, in order to prevent external interference, the ends of the pipes were immersed to the depth of about 3 inches in a vessel of water.

These arrangements must not be confounded with the attempts of some persons, both in this country and in France, to condense vapours which were supposed to rise in great abundance from fermenting liquids, and which are well known to have disappointed the expectations of the projectors. On two occasions, when the plan of condensation was tried by me, there was not any product, after passing the gaseous matter through a worm three quarters of an inch diameter and 35 feet in length, surrounded with water at a temperature of 54° for a period of 36 hours on each occasion.

Having arranged the improved tun as before described, the gas arising from six fermentations was allowed to escape through the water in the external vessel. After the gas had thus been washed it had lost much of the pungency of smell so characteristic of the usual mode of escape, and in a few days the water had so far changed, that it had a strong fœtid odour, similar to that of waste starch liquors, and certainly not that of the aroma of the hop. This, from the great difference between the water in question and that of the same bulk which had not been so treated, must have resulted from the absorption of a something passing off in mechanical sus-

pension with the gas. In order to ascertain the contents of the water after being charged with the gas and vapour, some of it was distilled, immediately after the transmission of the gas, and the result was, that from 36 gallons of the water so employed, 9 pints of alcohol were obtained of specific gravity 0·850. It appeared, on further prosecuting the matter, that more could have been obtained had a larger quantity of water been used, and that the action of the water on the gas depended for its efficacy, in a great degree, upon the apparatus itself. In endeavouring to realize more extended results a tub was made, which contained an arrangement of three tin plates perforated with holes, set one inch apart from each other, through which the gas passed in small bubbles, by which means the washing of the gas was rendered more effectual. In this manner 3 per cent. of rough spirit was frequently obtained, of specific gravity 0·850, by distillation from the gas produced by one fermentation. All these distilled products were impregnated with ammonia to a considerable amount, which would necessarily affect these results, as is shown by the following experiments.

45 gallons of water having received a charge of gas from the fermentation of 350 barrels of porter wort had a specific gravity 0·9988, and the attenuation of the worts during the period was about 12 lbs. per barrel, as indicated by the saccharometer of Dring and Fage. Of this quantity 36 gallons were reduced to one-sixth part by distillation, of which 16 oz. by measure were again carefully rectified and reduced to 4 oz., which had a specific gravity 0·965, being equal to 33 per cent. of alcohol at 0·825. It therefore follows that the 45 gallons would have yielded 15 imperial pints at 0·965, which would equal 5 pints at 0·825, or about 1·4 per cent. of alcohol by volume.

5 oz. of the original 45 gallons were distilled with baryta in excess, to combine with any acids that might be present, and the product was redistilled with hydrochloric acid; chloride of platinum and sodium was then added, and the whole carefully evaporated to dryness; the soluble parts having been removed by alcohol left 1·9 gr. of ammonio-chloride of platinum, which indicates by calculation 0·146 grain of ammonia. It follows, therefore, that 4·672 grains of ammonia were contained in the original bulk per gallon, or 210·24 grs. on the whole volume.

The residue, after the distillation with barytes, was examined for acetic and formic acids, but without success.

Respecting the volume of carbonic acid eliminated during the process of fermentation, I have not yet had the opportu-

nity of using an apparatus capable of measuring the amount set free from so large a quantity of wort as 180 barrels. On a small brewing of ale the quantity of gas measured by a very large metre was 7900 cubic feet. The meter having been charged with great care, the relative quantities were as follows:—43½ barrels of ale wort attenuated 16·5 lbs. per barrel, and gave off 7900 cubic feet of carbonic acid, or about 11 cubic feet of gas for every pound of attenuation. Again, 91 barrels of ale wort attenuated 15 lbs. per barrel, and gave off 11,700 cubic feet of carbonic acid, or about 11·66 cubic feet of gas for every pound of attenuation.

It being manifestly inconvenient to distil so weak a spirit on a large scale, from the necessity of apparatus and arrangements totally different from the usual machinery of a brewery, the means of preventing the saturation of the gas by the vapour of alcohol was the next object. This is accomplished in a most simple manner. The tun being air-tight, the exit-pipes for the carbonic acid were allowed to dip into a vessel of water to the depth of three feet, and by the pressure of the confined gas upon the surface of the fermenting worts the power of holding the vapour of the alcohol in the carbonic acid gas is checked, and a very large proportion of spirit thus retained, which would otherwise have been lost. The effect was tested as before by distillation, and although the retention was not complete, a most extraordinary reduction was made, amounting in some instances to 80 per cent. of the before-stated produce. The depth of 3 feet is of course an arbitrary number, but in practice a greater pressure is inconvenient from the difficulty of keeping large tuns air-tight by common means. The difference of the quantity of vapour dependent upon pressure will be confirmed by the following experiments, in addition to the test of distillation.

175 barrels of porter wort were fermented in a close tun, the exit-pipes of which were immersed in water to the depth of 3 inches. During the process, at three different periods, 100 cubic inches of the gas were passed through desiccating tubes, 17 inches long and half an inch in diameter, containing chloride of calcium, and on each occasion, for every 100 cubic inches, calculated as dry carbonic acid at a temperature of 52°, 0·425 grain increase of weight was obtained, due to the absorption of watery vapour.

181 barrels of porter wort fermented in the same vessel; the pipes being immersed 3 feet, gave the following result. For every 100 cubic inches, calculated as dry carbonic acid at a temperature of 52°, only 0·20 grain of vapour was absorbed. It would appear therefore that the vapour of water

given off during the process of fermentation bears directly on the proportion of alcohol carried away with the carbonic acid gas. If the simplicity of the arrangement is a ground for its recommendation, it must be evident that the foregoing apparatus would claim the attention of those conversant with the present system, as furnishing to the brewer a better control over his fermenting tuns, and the production of a stronger beverage from his worts.

I have much pleasure in acknowledging the material assistance afforded me by my friend Mr. Robert Warington in these investigations.

December 4, 1843.—The President in the Chair.

The following presents were announced since the last meeting:—

"The Pharmaceutical Journal," edited by Jacob Bell, from the editor.

A Specimen of Bitartrate of Potash in Fine Crystals, from J. Denham Smith, Esq.

Mr. Trenham Reekes was elected an Associate Member.

The following communications were then read:—

XC. *Note on a paper on Ferric Acid, read May* 16, 1843. *By* J. Denham Smith, *Esq.*

THE paper above referred to, which I had the honour of laying before the Society last session*, was unfortunately printed before I had proved that two material errors were contained in it. These errors arose partly from the almost invariable presence of manganese in the oxide of iron, precipitated from the sulphate, which I employed,—an impurity I neither suspected nor guarded against, and which usually occurs in such minute quantities as to render its detection impracticable by the ordinary tests; and partly from the solubility of sesquioxide of iron in potash under certain conditions,—a fact noticed by M. Chodnew†. The first error occurs in pp. 242—3, where it is stated that chlorine gas passed into "the deep amethystine solution of ferrate of potash, keeping the vessel cool during the passage of the gas, gives a solution of a lighter colour than the amethystine liquid." This solution proved to be a very dilute solution of permanganate of potash. I do not however find the intensity of colour altered by the gas, and from the permanent nature of this solution I hope eventually to succeed in isolating the potash salt.

The second is the more serious error (p. 247), where I an-

* See Memoirs, vol. i. p. 240.

† *Journ. für Prakt. Chemie,* Band xxviii.

nounced the existence of an oxide of iron forming a green salt with potash; such a salt I now believe does not exist. I prepared a quantity of this green solution by boiling ferrate of potash and rapidly filtering the clear green solution; this gradually decomposed, and the brown deposit was dissolved in hydrochloric acid, affording a yellow solution, to which a solution of hydrochlorate of ammonia was added, and then caustic ammonia; a small quantity of a reddish-brown flocculent precipitate, resembling sesquioxide of iron, fell; this collected, washed and redissolved in hydrochloric acid, gave a yellow solution styptic to the taste, which, diluted and rendered as neutral as possible, immediately struck the respective colours blue and blood-red, with ferrocyanate and sulphocyanate of potash, evidencing the presence of iron; the ammoniacal solution was evaporated to expel excess of ammonia, and tested with ferrocyanate of potash, when the voluminous flesh-coloured precipitate, characteristic of manganese, was produced: potash added to another portion of this ammoniacal solution gave, on the application of heat, a small quantity of the dark brown oxide of manganese.

Having, in the paper referred to, satisfied myself that iron did form a salt with potash, and also that the green salt contained this metal, I was too hastily induced to imagine that the colours, of the two solutions alluded to, arose from iron, not anticipating the existence of manganese in the precipitated sesquioxide of iron. Whether an oxide of iron, intermediate to the sesqui and teroxide, and possessing the qualities of an acid, really exists, I am at present unable to state, but hope to be able to decide this point, as well as to communicate some new facts respecting ferric acid and its combinations in a future paper.

XCI. *Observations on the Circular Polarization of Light by transmission through Fluids.* *By* H. B. Leeson, *M.D., A.M.*

IT is with considerable diffidence, and not without some regret, that I present the following observations on the circular polarization of light by transmission through fluids.

It is with diffidence, because the conclusions, which are the result of my own experiments, differ from those of others, deservedly considered able and acute observers. It is with regret, because the tendency of the facts, which I expect to establish before you, is to lessen in some degree the value of an otherwise beautiful application of optical science to the exigencies of chemical investigation.

It is equally important to detect that which is erroneous as it is to establish that which is true in science. Truth being my only aim, I trust that, whilst endeavouring to remove the veil of mystery and obscurity which has hitherto perplexed and thwarted many who, in common with myself, have assayed to follow out the experiments detailed by Biot and others, I may not be considered anxious to throw discredit on their labours; but candidly detailing the result of my own experiments, I can only say to them, as well as to others, "Si quid novisti rectius istis, candidus imperti; si non, his utere mecum."

The point in which the results of my own experiments disagree with those of other observers, is in regard to the alleged possession of *opposite* rotations by *certain* fluids, which have the property of deviating the plane of polarization of a beam of polarized light transmitted through them, some of those fluids being said to produce a *right*-handed rotation, others a *left*-handed rotation. On examining a great variety of samples of the *particular* fluids said to possess opposite rotations, I found that such fluids deviated the plane of polarization in only one direction, namely, towards the *right*-hand. The only fluids in which I have hitherto been able to discover a decided *left*-handed rotation is in the essential oil of lavender, and in that of cubebs*. The interesting fact, if true, that solutions of sugar, when obtained from different sources and in different conditions, possess in some cases a right-handed and in others a left-handed rotation, has not been corroborated by my own observations. When such solutions did exhibit any *decided* rotating influence, it was uniformly right-handed. It is, however, curious that solutions of cane-sugar differ from those of grape, potato and diabetic sugar in this respect; that whilst the former possessed a powerful rotating influence, the latter exhibited little or no rotating energy, although their solutions were in some cases sufficiently concentrated to furnish crystals after a few days' repose.

It might perhaps be supposed that such result proceeded only from my own want of information on the subject, or a deficiency of my powers of observation; indeed, I long so considered it myself, so much so, that, not satisfied with obser-

* The amount of left-handed rotation in oil of cubebs is much greater than that of oil of lavender. This oil, which was colourless, and some others contained in the table accompanying this communication, have been examined since my paper was read, the samples having been kindly furnished by Mr. Warington of Apothecaries' Hall. Samples of oil of cubebs obtained elsewhere were coloured, and possessed much less rotating energy, being probably adulterated with oil of peppermint.

vations made with apparatus procured in this country, I commissioned a friend to procure for me from Mons. Soleil of Paris an apparatus made according to Biot's own directions. Experiments made with that instrument confirmed the conclusions I before arrived at, and I may add, that an examination of the apparatus itself has in some degree suggested the possible sources of error.

I do not of course positively assert that the observations of others have been erroneous, although strongly inclined to suspect they may have been misled. Nothing but an examination of the *same* sample could indeed establish such conclusion. I have never, however, been so fortunate as to obtain a solution of sugar possessing a decided *left*-handed rotation; and although it is certainly possible that the oil of lemons or oil of turpentine which I have examined may differ from that experimented on by others, still I have tried so many samples, warranted genuine and procured from so many different sources, that I can scarcely imagine it possible to procure samples possessed of opposite rotating powers; I may also remark, that although I have observed variations as respected the amount, I have never noticed any variation as respected the *direction* of rotation in any of the samples of the same description of fluid.

Misunderstanding may perhaps result from the converse use of the terms *right*- and *left*-handed rotation by different writers, but this cannot affect the essential fact, if true, that oil of lemons, for instance, has an opposite rotation to that possessed by oil of turpentine, or the still more interesting fact alleged, unfortunately, I fear incorrectly, that a solution of sugar as existent in the juice of grapes rotates the plane of polarization in an opposite direction to that in which it is rotated by a solution of sugar obtained from the cane.

The direction to which, in common with other writers, the term right-handed is subsequently applied cannot be mistaken by those who attend to the instructions hereafter given, and I would recommend every one previously to experimenting on fluid substances, to study the opposite appearances presented on analysing polarized light when transmitted through specimens of right- and left-handed quartz, as usually sold for illustrating circular polarization, and as exhibited in Plates III., IV., V. and VI.

With a view to the more explicit understanding of the mode in which the experiments referred to have been conducted, and to assist those not conversant with the subject in repeating them for themselves, I shall very briefly explain what is meant by the deviation or rotation of the rays of polarized

light when transmitted through fluids said to possess circular polarization.

Assuming the general principles of the undulatory theory of light, and making use of terms which, if not absolutely correct, are at least convenient, I shall first advert to what is meant by *rectilinear*, or, as I would suggest it should be termed, *rectangular* polarization.

When a beam of ordinary light impinges on a polarizing medium, it may be considered as dividing itself into two portions, the waves of which respectively undulate in directions varying from each other 90°, *i. e.* a right angle, in other words, they are said to possess opposite planes of undulation, and to be rectangularly polarized*. This effect may be produced by five different modes, viz. refraction, reflexion, absorption, dispersion, and double refraction.

A number of pieces of thin glass † superimposed on each other, and inclined at a suitable angle to a ray of light incident thereon, polarizes one portion of the light transmitted through it by refraction, whilst the other portion reflected from the surface is also polarized, but in an opposite direction. That the two portions into which the light is thus divided are oppositely polarized, or may be supposed to undulate in opposite directions, is established by the fact, that if transmitted towards a similar bundle of glass, the two rays would comport themselves differently; that is, they would not both be reflected or both transmitted by such second bundle if held in the *same* direction or plane towards each respectively. Calling the one portion of polarized light into which the original beam of ordinary light R (figs. 1 and 2, p. 30) is divided O, and the other portion X, it will be found that the position of the second bundle necessary to reflect X must be at right angles to that in which it would reflect O, and similarly as to refraction or transmission. This second bundle serving to distinguish the two rays, is termed the analyser. Figs. 1 and 2 serve to illustrate polarization by refraction and reflexion. In fig. 1 the bundles of glass are supposed to be all in the same plane, or situated parallel to each other, whilst in fig. 2 the bundles B and C are supposed to be situated at right angles to the bundle A. The beam of light R impinging on the bundle A is divided into two portions, O and X; and

* Consideration of the direction in which the waves of light may be supposed to undulate will materially assist the memory in studying the facility of reflexion or transmission of the respective rays by surfaces opposed to them in different positions.

† The very thin glass sold for covering microscopic objects is extremely convenient for this purpose.

it will be observed that O, proceeding in its original course, is transmitted or passes through the second bundle B, fig. 1, whilst X is reflected from, and does not pass through, the bundle C. The converse takes place in fig. 2. Hence it will be observed that in fig. 1 the portion O is capable of

Fig. 1.

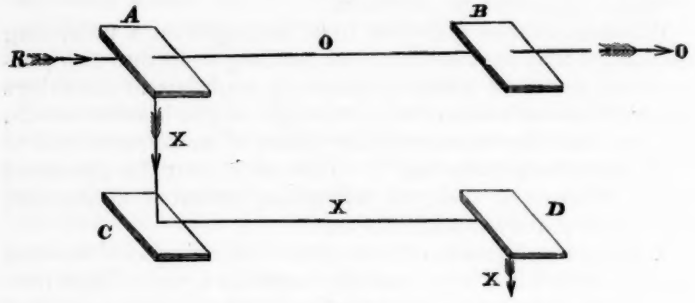
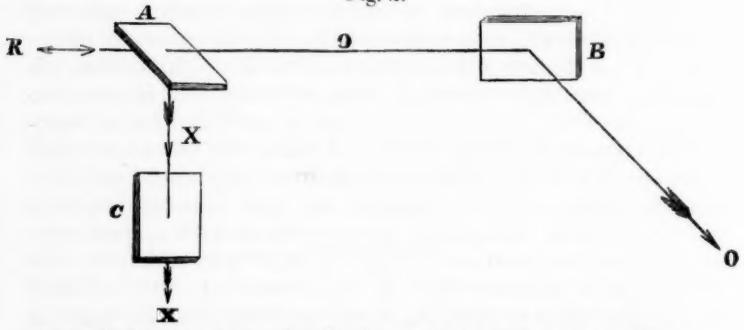


Fig. 2.



transmission but not of reflexion, whilst the portion X is capable of reflexion only. In fig. 2, where the bundles B and C are supposed to be placed at right angles to the bundle A, the portion O is capable of reflexion only, and X of transmission. In these figures A forms what is termed the polarizer, whilst B, C and D are what are termed analysers, serving to test the condition of O and X.

A tourmaline effects a similar division of a beam of light impinging on it into two portions oppositely polarized, transmitting one, say O, in one position, whilst X is absorbed: revolving the tourmaline 90°, X will be transmitted and O absorbed. For experiments on circular polarization, as well as for microscopic purposes, the green tourmalines may be recommended, as they can be more easily obtained free from flaws. When of a proper thickness and ground truly parallel, they form excellent analysers to apply to the eye-pieces of

microscopes; for experiments on circular polarization they form very useful polarizers. The blue, yellow and hair-brown tourmalines are perhaps superior when free from flaws, but cannot be so readily obtained perfect.

Agates polarize by dispersion, but are not suitable for experiments on other substances.

Iceland spar and quartz polarize light by double refraction. The beam of light transmitted through them is divided into two portions, O and X, polarized in opposite planes, but proceeding in paths so closely posited, that they may both be the subject of observation at the same time. This is not the case however in what are termed Nicholl's prisms, which are purposely so constructed as to allow only one portion to be transmitted when held in one direction, whilst the other is transmitted when the prism is revolved a right angle. The rhombs of Iceland spar are usually rendered achromatic by cementing a piece of glass properly adjusted to them. In order to render quartz available a particular construction is necessary, but when well made double refracting analysers of quartz are equally useful for these experiments.

It does not matter by what means our polarized beam is first obtained, or in what manner the same is analysed, or whether one mode be used to polarize the light and another to examine or analyse the same. In all cases the result will be dependent on the relative positions of the polarizer and analyser, and if these are placed in such a direction to each other as that X is not transmitted to the observer's eye, and therefore dark, then O will be transmitted; but if either the analyser or polarizer is changed to a position exactly at right angles to its former direction, then O will be obscured, whilst X becomes light. When one portion has obtained its greatest obscuration, or is invisible, the other will have obtained its maximum of illumination, whilst they pass gradually from one condition to the other at the intermediate positions *, as represented in Plates I. and II.

* A most convenient mode of obtaining polarized light which occurred to me about two years ago, and which I have since shown to several friends, consists in placing an ordinary looking-glass on the outside of a common window, the bottom of the mirror being placed close to the lower portion of one of the panes of glass, whilst the top is inclined from the window towards the sky, so as to reflect the pane of glass into a horizontal position. Standing then within the apartment, and looking through a tourmaline or other analysing medium at the light of the sky reflected from the mirror through the pane of glass, it will be found intensely polarized, and on introducing any substance, such, for instance, as a fluid contained in a glass tube or a crystal, &c., between the analyser and the polarizer, it may be readily examined. The great advantage of this mode of obtaining polarized light consists not only in the perfection of the polarization, but also

On using as an analyser a rhomb of Iceland spar, or a prism of quartz constructed as before alluded to, the oppositely polarized beams of light, O and X, may be observed together, and they will become alternately light and dark as the analyser is revolved, according to the law already laid down. This may be understood by revolving the outer circle of Plate II. whilst the lower moveable circle* remains stationary. The ordinary ray being represented by O, and what is termed the extraordinary ray by X, the rhomb or prism should be so arranged or posited in its setting as that O be central, and therefore apparently stationary, whilst X revolves around O†, as the analyser is itself rotated, as represented in the different Plates exhibiting the successive changes in the appearance of a polarized ray of light transmitted through a small circular aperture, and analysed by double refraction. This may be also understood by revolving the outer circle of Plate II., as before stated, by which it will be seen that each portion, O and X, returns to its original condition after a revolution of half a circle, or 180°, and that it passes from the state of greatest obscuration to that of maximum illumination on a rotation of 90°, or quarter of a revolution.

In all these cases, then, of what is termed *rectangular* po-

in the extent of the field of view, which is a great advantage in examining large specimens, such as unannealed glass, although not so important in circular polarization.

I may here observe, that the sky at all times furnishes polarized light, which is more or less intense according to the relative position of the observer and the sun. This circumstance probably influences the chemical action of the rays of light, and points out the necessity of varying the position of the camera, or the period of exposure in taking Daguerreotypes and other optical investigations, according to the time of day, the state of the sky, and the sun's declination. Any person may readily ascertain where the greatest intensity of polarization exists by using a tourmaline, or other analysing medium, and looking through it at a piece of selenite, or a piece of Iceland spar or other crystal, cut to exhibit the cross and rings; of course the colours will be most vivid, and the black cross most intense, where the greatest polarizing force exists. This polarization is most intense where the sky is blue and unclouded. The planes of polarization appear to vary at a total distance of 90°, or of 45° measured each way from the sun's position.

* In Plates II., V. and VI. the lower moveable circle is introduced as a means of imitating the supposed deviation in the plane of polarization by moving it to the right-hand or to the left in Plate II., and by moving it to the left in Plate V., or to the right in Plate VI. The outer moveable circle in all the Plates represents the rotation of the *analyser*.

† This is very important to prevent confusion arising from a revolution of the two images around each other, whereby the one may be mistaken for the other. In Plates II., V. and VI. it is manifest that the exact centrality of the ordinary ray could not be preserved as in using the apparatus itself.

larization, the maximum of illumination takes place when the analyser is placed with its plane of polarization corresponding to that of the ray to be transmitted, whilst such ray attains its greatest obscuration when the analyser is placed at right angles to such plane. Now this condition is altered when a medium of a certain thickness *, possessing what is termed *circular* polarization, is introduced between the polarizer and analyser; for if the polarizer and analyser be placed so that one ray, X, is at its greatest obscuration or invisible, and the other, O, at its maximum of illumination, as represented at 0° in Plate I., and as also shown when the indexes of the moveable circles in Plate II. are both pointed to 0°, then on introducing a circularly polarizing medium between the analyser and polarizer, the plane of polarization will be removed to the right-hand or to the left, which may be imitated by moving the index of the inner circle (Plate II.) in either of those directions, whilst the outer circle continues stationary: and it will be observed that, in consequence of such change in the plane of polarization, X will become lighter and O darker, and that the outer circle, which may be supposed to represent the analyser, must be revolved an equal number of degrees in the same direction as the inner circle, in order to restore X and O to their primary condition. When the rotation of the analyser *proceeds in the direction of the numbers in the outer* circle of graduation, the rotation is termed *right*-handed, when in that of the *inner* circle *left*-handed.

Supposing the rotation produced be 30° to the right; place the index of the inner moveable circle at 30° on the outer circle of graduation; then the other moveable circle or analyser must be also shifted 30° to the right-hand, in order to obscure X; proceeding onwards, it will be observed that X becomes bright at 120°, being a further revolution of 90°; again becomes obscured at 210°, or a revolution of 180°, and again bright at 240°. On registering, then, the degrees at which O and X are respectively polarized, that is, most obscured, we have the following table:—

X	O	X	O
30°	120°	210°	300°

the degrees being observed on the outer or right-handed circle of graduation, and corresponding to

X	O	X	O
330°	240°	150°	60°

on the inner or left-handed circle of graduation. Had we

* A certain thickness is here stated, because, as will be hereafter shown, it is possible in every case to employ a thickness which would produce no apparent alteration.

moved the analyser or moveable circle in a left handed direction, we might have registered our results as follows:—

O	X	O	X
60°	150°	240°	330°

by which it will be seen that it would be impossible, from the appearance presented at any given position, or the direction in which the analyser was revolved, alone considered, to say whether the deviation was 30° to the right or 150° to the left; and this would of course be equally true of any other amount of deviation.

To add to the difficulty, the deviation is in direct proportion to the thickness and nature of the circularly polarizing medium. If you find, for example, a deviation of 10° produced by a medium of 1 inch in depth, a depth of 10 inches would produce a deviation of 100°; so that by merely varying the thickness or depth of the medium, you may have the position of greatest obscuration situated in *any* part of the circle, and if the thickness happened to be such as that such position coincided with 180° or 0°, you might suppose that the medium was not possessed of circular polarization at all; the importance, therefore, of examining different depths or thicknesses will be apparent; and the depth of each medium which produces a deviation of 180°, furnishes a very useful index of their comparative circularly polarizing energy.

If the depth be constant and two circularly polarizing liquids be mixed together, or if the fluid or substance be dissolved or mixed in some other fluid possessing no rotating energy, the deviation will bear a direct relation to the proportion in which the two are combined. For instance, since, according to my own experiments, 10 inches of a solution of cane-sugar in water containing half its weight of solid sugar produces a deviation of 104°, on mixing such solution with an equal bulk of water, 10 inches of such diluted solution would produce a rotation of only half that amount, or 52°, which coincides with experiment; having, therefore, once obtained the rotating power of a solution of given strength, we may, according to Biot, calculate thence the strength of any other solution when examined in a similar manner; attention, however, must be paid to the effects of temperature, any condensation which may take place on mixture, specific gravity, &c.; and I have not found the result of experiments quite accord with those of calculation, although the difference has been but slight, and this is probably due in some degree to the circumstances hereafter mentioned.

The rules of proportion do not directly apply to the percentage of sugar by weight contained in solution, unless the

specific gravity and bulk be likewise taken into account. For instance, the solution referred to was prepared as follows:—

1000 grains dry sugar,
1000 ... water,

and its specific gravity was 1·2371; consequently 1 gallon of such solution would weigh 96,597 grains, and contain 48298·5 grains sugar. Now since 10 inches of such a solution produced a rotation of 104°, on adding an equal bulk, that is, another gallon of water to the original gallon, 10 inches would produce a rotation of 52°; but 1 gallon of water weighs 70,000 grains, which added to the weight of the syrup, 96,597 grains, gives the weight of 2 gallons, 166,597 grains, supposing no condensation to arise from the mixture; consequently 1 gallon of the new solution would weigh 83298·5 grains; and since it contains half the original quantity of sugar, or 24149·25 grains, the proportion by weight will be 24149·25 sugar to 59149·25 water, since 24149·25 + 59149·25 = 83298·5; so that the proportion of sugar by weight to the water is less than one-half, which would have been the case were the rotation in direct proportion to the weight of sugar as compared with that of the water in which it is dissolved, without reference to the bulk occupied by the mixture.

Again, if the proportions of the combination be constant, but the depth varied, the degrees of rotation will, as before stated, bear a direct proportion to the depth; thus, since 10 inches of a solution of cane-sugar, containing one-fourth its weight of solid sugar, produces, according to my experiments, a rotation of 50°, if the depth be 1 inch it would produce a rotation of 5°, and 36 inches would produce a rotation of 180°, and consequently with such a depth there would be no apparent rotation.

Having thus shown that neither the direction in which the analyser is rotated, nor the appearances presented at any given point, can alone enable us to determine whether the rotation is right or left-handed, we proceed to explain that such information can only be obtained by observing the order of succession in which the different tints or shades of obscuration present themselves.

Removing the index of the inner moveable circle (Plate II.) any number of degrees not exceeding 90° either to the right or to the left, it will be readily observed that the direction in which it has been moved might be ascertained by observing whether on moving the outer circle or analyser the image X became darker or brighter; the image X becoming darker when the outer circle or analyser is moved in the *same* direction as the other, but lighter if moved in an opposite direction. This law, however, it will be also seen is reversed if

the rotation exceeds 90°. This method, then, affords the means of ascertaining the direction of rotation, *provided* it does not exceed 90°; the rotation being *right*-handed, if, when the analyser is *turned to the right-hand*, the image which is the subject of observation becomes darker and darker, and *left*-handed if it becomes lighter.

It matters not whether X or O be the subject of observation, or whether X be light and O dark when set to 0°, provided the amount of rotation be estimated from the position necessary to restore either ray to precisely the same condition in which it appeared at 0°, *previously* to the introduction of the circularly polarizing medium. When, however, a double refracting analyser is used, I would in all cases recommend the experiment to be commenced by placing the analyser and polarizer in such a position as that X is at its greatest point of obscuration when the vernier or index points to 0°, and as represented when the indices of the two moveable circles of Plates II., V. and VI. are both at 0°. When a Nicholl's prism or tourmaline is used as an analyser, presenting only one image, then, previous to the introduction of the circularly polarizing medium, it must be so placed with respect to the polarizer as that the index of the vernier points to 0° when the light is most completely polarized or obscured. Uniformity in the mode of conducting these experiments will greatly promote accurate results.

To return, however, to the means by which the direction of the rotation is to be ascertained. The method already described might be applied in examining solutions of weak rotating energy which exhibit little or no colour when examined by polarized light, provided it is not confounded with the effects of mere depolarization, the appearances then presented being similar in some respects to those produced by double refracting substances, as described in the twenty-first chapter of Brewster's Treatise on Optics. When substances of greater energy are examined, they exhibit a gradation of colours corresponding to those of the solar spectrum, which affords a still more satisfactory mode of determining whether the rotation is right- or left-handed. The direction corresponds to that in which the analyser must be moved in order to obtain the succession of colours as follows, viz. red, orange, yellow, green, blue, indigo, violet. If the analyser be moved in only one direction, and that right-handed, or in the order of the figures in the outer circle of graduation, then the rotation will be right- or left-handed, according to the succession of the colours in the following tables, represented in Plates III. and IV. The general order of succession when the *analyser* is moved in a *right*-handed direction is first given, viz.

Left-handed.			Right-handed.	
X.	O.		X.	O.
Violet	Yellow	0°	Violet	Yellow
to	to	to	to	to
Green	Orange	45°	Orange	Green
to	to	to	to	to
Yellow	Violet	90°	Yellow	Violet
to	to	to	to	to
Orange	Green	135°	Green	Orange
to	to	to	to	to
Violet	Yellow.	180°	Violet.	Yellow.

The following table gives a more detailed account of the succession of tints produced, and commences, it will be observed, with the boundary of the blue and violet, which is the darkest ray, corresponding to the greatest obscuration of X, and is the point at which the degree of rotation should be observed. We may derive much assistance in estimating its precise position, when a double refracting analyser is employed, by examining the appearance of O, which will then be at its maximum of illumination and of the brightest and purest yellow tint. When we travel too far into the violet with X, O will assume a greenish-yellow tint; when too far into the blue, the yellow will deepen towards an orange. If a tourmaline or coloured polarizer be employed, attention must be had to its effects upon the yellow ray, which may be easily ascertained by observing the appearance of O previous to the introduction of the circularly polarizing medium.

Left-handed.			Right-handed.	
X.	O.	°	X.	O.
Blue violet.	Bright yellow.	0	Blue violet.	Bright yellow.
Blue.	Deep yellow.	10	Violet.	Greenish yellow.
Greenish blue.	Orange yellow.	25	Crimson.	Pale green.
Green.	Orange.	35	Reddish orange.	Light green.
Light green.	Reddish orange.	50	Orange.	Green.
Pale green.	Crimson.	65	Orange yellow.	Greenish blue.
Greenish yellow.	Violet.	80	Deep yellow.	Blue.
Bright yellow.	Blue violet.	90	Bright yellow.	Blue violet.
Deep yellow.	Blue.	100	Greenish yellow.	Violet.
Orange yellow.	Greenish blue.	115	Pale green.	Crimson.
Orange.	Green.	125	Light green.	Reddish orange.
Reddish orange.	Light green.	140	Green.	Orange.
Crimson.	Pale green.	155	Greenish blue.	Orange yellow.
Violet.	Greenish yellow.	178	Blue.	Deep yellow.
Blue violet.	Bright yellow.	180	Blue violet.	Bright yellow.

The following general conclusions will be easily understood from the Tables, as well as by an examination of Plates III.

and IV., and also of Plates V. and VI., where any amount of rotation may be imitated by moving the index of the respective inner moveable circles, as before explained in regard to Plate II.

That, whether the rotation be *right*- or *left*-handed, the *order* of succession of colours is the *same in* X as it is *in* O, the one lagging as it were 90° behind the other.

If the analyser be revolved so as to obtain what may be termed a *descending* succession of colours, viz. red, orange, yellow, green, blue, &c., the *direction* in which it is revolved *corresponds* to that of *rotation*.

If the analyser be revolved to the *right*-hand when examining a substance possessed of *left*-handed rotation, the order will be in what may be termed an *ascending* scale, viz. blue, green, yellow, orange, red.

If in examining a substance possessed of *right*-handed rotation the analyser be turned to the *left*, the order will also be in an *ascending* scale, viz. blue, green, yellow, orange, red, &c.

That, *whether* the rotation be *right* or *left*, provided the amount is alike, X and O will exhibit the *same tints* at a *similar number* of degrees of rotation marked in the right- or left-handed circles of graduation respectively.

Hence, at the points of greatest obscuration, there is *no* difference in the appearances exhibited, whether the rotation be *right*- or *left*-handed.

That X assumes the tint of O, and O that of X at an exact interval of 90°. This is particularly apparent in Plate IV., in consequence of the juxtaposition of the colours.

That with a double refracting analyser each particular tint occurs four times in the course of a complete revolution of 360°, viz. twice in the ordinary, and twice in the extraordinary ray. With a tourmaline or a Nicholl's prism, the tints will of course occur only twice in a whole revolution.

That in a revolution of 180° the tints have passed through all their phases.

The tints that have been described, and which are represented in the Plates, correspond to those of quartz, and are more or less vivid in proportion to the rotating energy. In fluids the blue violet generally assumes more of a neutral tint, and in many instances the crimson is scarcely to be observed. Of course, if the fluid be itself possessed of colour, it will greatly interfere with the purity of the tints. When using a piece of red glass, as recommended by Biot, to obtain homogeneous light, the tints disappear, and the obscuration of X, which is then more complete, will determine the amount of rotation. The red glass sent by Mons. Soleil with Biot's ap-

paratus is much too dark, and occasions so great a loss of light as materially to interfere with the delicacy of our readings. Of course the *direction* of the rotation should be observed *without* it.

Daylight is preferable to artificial light for these experiments; unless, as before explained, in the case of a coloured polarizer, attention is paid to the appearance of O when artificial light is employed, the results will not agree with those obtained by daylight.

Having explained the appearances which are to guide our experiments, I proceed to a description of the apparatus which I constructed for the purpose, and which is similar in some respects to the arrangement of the Rev. B. Powell, described in the Philosophical Magazine for April 1843.

M N O P (figs. 1 and 4, p. 40) is a wooden box, the lid of which *b b* not only opens in front, but may be also fixed at any height, and fastened by a small bolt at *a*, fig. 1. This box serves the purpose of a darkened chamber, and the apparatus may be packed in it when not in use. K K is a moveable perforated shelf, which may be also secured at any height by means of the screw at I, fig. 1, passing through an opening in the back of the box shown at X, fig. 4. On this shelf the vessel containing the fluid to be examined is to be placed, its centrality being provided for by fitting into another loose shelf turned out to suit it. To the under side of the shelf K a brass plate is screwed, fitted with a socket to receive the polarizer G, which may be either a tourmaline or a Nicholl's prism, and which may be revolved by means of the collar attached to it for that purpose. H is a mirror to reflect the light through the polarizer and liquid towards the analysing double refracting eye-piece A B C D, fig. 3, and A, figs. 1, 2 and 4. This eye-piece consists of a lens C placed at its focal distance from a small aperture at D, so as to give a well-defined image of it when transmitted towards the observer's eye at A; B is a double refracting achromatic analyser of Iceland spar, or of quartz, which is placed within a tube which slides into the tube containing the lens, and also fits into the socket of the vernier, it being sometimes desirable not to use the lens. A Nicholl's prism, or a tourmaline similarly fitted, may occasionally be substituted. This analysing eye-piece fits tightly into a socket adapted to the vernier E of a circle F, fig. 2, graduated as in Plates II., V. and VI. The analyser may be adjusted by turning it in its socket, and when set to its proper position revolves with the vernier. The graduated circle, with its vernier and eye-piece, is attached, for the convenience of removal in packing, to a loose shelf L L, and is

always secured in the same position by steadying pins. The upper end of the box has a circular opening of about $1\frac{1}{2}$ inch diameter, which serves to centralize and steady the tube passing through it, as shown in fig. 1. S T V, fig. 1, is a three-

Fig. 1.

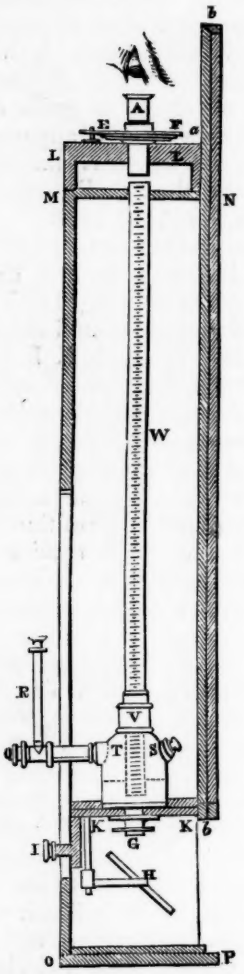
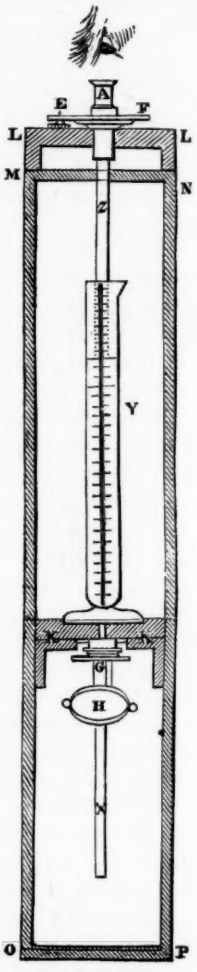


Fig. 2.

Fig. 3.

Fig. 4.



necked glass vessel to contain the liquid to be examined. W is a tube graduated into inches and tenths, passing through an air-tight, brass stuffing box, cemented to the vessel at V. S is an opening fitted with a stopper, which is useful in filling, emptying and cleansing the vessel. R is a small condensing

air syringe adapted to the vessel at I, and Q is a brass screw, for the purpose of allowing the air to escape when requisite. The method of using the apparatus is as follows:—First, secure the shelf at the proper height to receive the vessel to be subsequently introduced, then adjust the mirror to reflect the light, of the sky or a lamp, upwards towards the analyser at A, set the vernier to zero on the graduated circle, then place the analysing eye-piece in the vernier, so that the extraordinary image X is also directed towards zero; next revolve the polarizer G until X has attained its maximum of obscuration, taking care not to disturb the vernier or mirror. The apparatus is thus ready for experiment, and the liquid to be examined must next be introduced. It may either be contained within a glass vessel, S T V, such as we have already described, or in a simple graduated glass tube, as shown at Y, fig. 4, in which case the brass tube Z, blackened on the inside, and fitted on to the lower part of the analyser, is occasionally useful, and lessens the necessity of closing the door to obtain a darkened chamber. The bottom of either vessel should be very transparent and free from irregularity or specks. These vessels are to be placed upon the shelves, as shown in the drawings, and the door of the box closed. The vessel S T V is contrived for the purpose of examining different depths of the same liquid without removing the vessel, which is necessary when using only a simple tube, as shown at Y, fig. 4. By condensing air into the vessel by means of the small syringe, the liquid may be raised to any height in the tube W, and it may again be lowered by allowing the air to escape at the screw I. The liquid having been introduced, suppose within the vessel S T V, and occupying a depth, say of 2 inches, the image X, which was invisible before, will then, in all probability*, become apparent and tinted, if not decidedly so, raise the liquid by means of the syringe until it does, and observe the depth; then move the vernier in a right-handed direction until the image X attains its maximum of obscuration, and read off the amount of rotation; continue the movement of the vernier until O next becomes obscured, then again observe X, and then again O. Thus you will obtain four readings corresponding to the depth observed, each of which should differ from the preceding 90° if your observations have all been correct, but if not, a mean must be taken, and it will in all cases be better to take a mean of several observations, and again to compare such mean with that obtained from an observation of the height necessary to rotate

* Alluding to the accidental circumstance of the depth corresponding to 180° rotation.

the ray 180°, which is procured as follows:—Having placed the vernier so that X is at its greatest point of obscuration, and observed the height at which the liquid stands, pump in air to raise the liquid until O becomes most obscured, and observe the additional height necessary to effect this, corresponding to a rotation of 90°; continue the raising of the liquid until X again becomes obscured, and again observe the additional height, which, if the experiment be correctly conducted, should be equal to the former, and of course the total height will correspond to a rotation of 180°. It is unnecessary to say anything more about the mode in which the direction of the rotation is to be ascertained, this having been already fully explained. I shall conclude, therefore, with a few further observations on sources of error which may tend to mislead or to interfere with the accuracy of observations. When examining different heights care must be taken that the fluid which adheres to the sides of the tubes has time to subside, otherwise the apparent amount of rotation will be thereby increased.

Great care must be taken that the position of the mirror is not altered after the adjustments are made, as with some Nicholl's prisms I have found a very slight change of the inclination of the mirror altogether alter the plane of polarization.

After the adjustments are made, any double refracting medium placed upon the shelf will cause the image X to become depolarized and therefore luminous; this must not be confounded with circular polarization, which I suspect has been the case. Many oils, and some solutions of grape and potato sugar, exhibit this phænomenon. The difference from circular polarization will be readily understood by attending to our former instructions, and observing that in these cases there is no alteration of the *position* of the plane of polarization exhibited on rotating the analyser, more especially on increasing the depth of the liquid; I would strongly advise any one experimenting on this subject to examine the appearances presented by pieces of unannealed glass, crystals, mica, selenite, &c., by placing them upon the shelf K K when the apparatus is adjusted. I should however observe, that some specimens of unannealed glass, mica and selenite, possess circular polarization as in quartz, and it probably exists to a much greater extent than has been hitherto noticed.

Water cooled below 39° is a curious example of the phænomenon last alluded to, which I discovered about three years since, but did not then feel sufficiently satisfied with the mode of observation. I have now completely verified the fact, which may be readily exhibited by means of the apparatus now described. Since this paper was read I have however obtained

apparent evidence of rotation, amounting to about 15 degrees for a depth of 15 inches, but rapidly disappearing as the temperature of the water rises. I am about repeating these experiments, and shall communicate the result in a future paper.

When a Biot's apparatus, as constructed by Mons. Soleil, is used, mistakes may arise, not only from the confusion of the extraordinary and ordinary images revolving round each other, before alluded to, but also from the graduation of the circle, which is divided to 180° on either side of 0° and no further. Supposing, for instance, a rotation of 79° to the right, since on moving the vernier 11° to the left the obscuration of O would be observed, it might be mistaken for a left-handed rotation of 11°. Probably some such error occasioned Subeiran to state that a solution of sugar which showed an original rotation of 71°, was altered after boiling as in the following table.

Primitive syrup	71° right-handed.
After 20 hours	0
... 25	11° left-handed.
... 64	0
... 74	5° right-handed.

Supposing Subeiran mistaken as to the direction of the rotation (and he tells us nothing of the succession of tints by which it might have been determined), but correct as to the points of obscuration, his statements would lead us to infer that it was really a right-handed rotation throughout, but increasing, as it naturally would do, from + 71° to + 95° as the water evaporated. The difficulty of determining the exact reading, which requires much practice, will readily account for an error of a few degrees, and the subjoined table (based on the supposition that the original bulk was preserved as it ought to have been by the addition of as much water as was lost by evaporation) will show that in the last four experiments O_2 was probably mistaken for X.

Yellow ray, depth 100 *millimetres* = 3·937 *inches.*

	Subeiran.	X.	O.	X_2.	O_2.
Primitive syrup	+71	71°	161°	251°	341° = − 19
after 20 hours	0	90°	180°	270°	360° = 0
... 25 ...	−11	79°	169°	259°	349° = − 11
... 64 ...	0	90°	180°	270°	360° = 0
... 74 ...	+ 5	95°	185°	275°	365° = + 5
		5)425°	5)875°	5)1325°	5)1775°
Means ...	.....	85°	175°	265°	355° or − 5

The above table will give a general idea of the mode in which the results are to be taken and tabulated. I find, as might be expected, that solutions of sugar become decomposed by keeping and by heat, but the effect is simply to diminish the amount of rotation, and not to alter the direction. I have already adverted to the care required in observing the precise point of obscuration, viz. the extreme boundary between the blue and violet ray, and to the assistance to be derived from observing the complementary tint.

It is desirable to preserve one position during the observations with the face towards zero, and to look steadily in a perpendicular direction, as the appreciation of the tint will vary somewhat if the position of the eye be altered*. I generally get an assistant to note the numbers, so that the observations may be made with as little looking off as possible. The effect of gazing at all coloured objects must be remembered, and it would be well to have the whole of the apparatus blackened, or, where convenient, to make the observations in a darkened chamber. The loss of light occurring from an increased depth or strength of liquid, especially if such liquid be coloured, must be also considered, and will frequently prevent the experiments made at different depths from according as they should do with each other. With constant practice I can obtain a reading to half a degree, beyond which I do not think it is possible in most cases to obtain any certainty; and of course the method does not furnish an accurate substitute for chemical analysis, although it may be useful as a rough mode of appreciating the purity of an oil or the strength of a solution of sugar.

I subjoin a table of the results of some experiments, and shall have great pleasure in examining any other samples that may be sent or brought to me at the Laboratory at St. Thomas's Hospital.

Table of some rotating Liquids.

Right-handed.

	Depth 10 inches.	180° rotation.
Essential oil of caraway .	200°	9 inches.
... ... dill . . .	190°	9·5 ...
... ... lemon . .	150°	12 ...
Rectified oil of turpentine .	50°	36 ...
Common oil of turpentine .	40°	45 ...
Essential oil of nutmeg . .	33·5°	53·46 ...
Solution of 1734 grs. camphor in 2105 grs. alcohol	52°	34·5 ...

* With some analysers the plane of polarization will be entirely changed if the position of the eye be greatly altered.

Solutions of cane-sugar in cold distilled water :

Equal weights, sp. gr.	1·2371	104°	17·307...
1 sugar to 2 water	1·1473	70°	25·7 ...
1 sugar to 3 water	1·107	50°	36·0 ...

Left-handed.

	Depth 10 inches.	180° rotation.
Essential oil of cubebs . .	83°	21·8 inches.
... ... lavender .	20°	90 ...

Table of Essential Oils examined and possessing no rotating energy.

Essential oil of anise.
... ... cloves.
... ... pimento.
... ... chamomile.
... ... calamus.

December 18, 1843.—The President in the Chair.

A Specimen of Catechuic Acid was presented by John Thomas Cooper, Esq. to the Society's Museum.

Robert Kane, Esq., M.D., Amos Swaisland, Esq., Thomas Jennings, Esq., Andrew Muter, Esq., James Millar, Esq., and David Waldie, Esq., were elected Members; and Messrs. Robert Hunt and John Mercer, Jun., as Associates of the Society.

The following communications were then read :—

XCII. *Observations on Catechuic Acid.* *By* John Thomas Cooper, *Esq.*

A SHORT time since I was requested to visit a tannery where the principal tanning ingredient employed was catechu, and among other matters my attention was directed to a whitish substance which made its appearance on the external surface of the leather when the tanning process was completed, and the uniform appearance of this substance over the whole surface is considered by the proprietors as the test of the perfection of their process of tanning, which is usually accomplished in about fourteen days. The tanning liquor is prepared by making an imperfect solution of the catechu in warm water, or in the liquor that has been previously partially exhausted of its tannin by a former operation; the depilated hides in their usual state are sewn up so as to form water-tight bags, into which the tanning liquid, prepared as above, is placed, so as to completely fill them; they are then placed on floors and turned once or twice a day into every

possible position to expose the hide as equally as possible to the action and pressure of the tanning liquid, and as the process of tanning advances the appearance of this white matter becomes more and more evident, until at length it covers the entire surface of the leather, and sometimes acquires considerable thickness and solidity. In this state, however, it is contaminated with many impurities, and after repeated trials to obtain it in a state fit for examination, I found the following simple method to answer the purpose I had in view very well. The matter, as obtained by scraping from the surface of the leather, was thrown on a filter of linen cloth and washed with cold water until the water passed through very nearly colourless; by this means a quantity of tannin, mucilage, extractive matter, and a peculiar substance, which I have not yet examined, were removed; the matter remaining on the filter was then treated with hot water, either by washing it on the filter, or which is better, by removal into a basin and heating it with three times its bulk of water to near the boiling point, when a brown-coloured solution was obtained, and by filtering this while hot in a warm place, the substance which has the characters of catechuic acid, catechine, or tanningenic acid is deposited as it cools, but the deposition of the whole I find does not take place until many hours after it has become cold, therefore, after a lapse of about twenty-four hours, it may be thrown on a filter and washed with cold water, in which it is nearly insoluble, until the water passes through colourless, or very nearly so, and then dried slowly by exposure to a gentle heat; in this manner the specimen herewith presented to the Society has been prepared, and which, if examined, will be found to possess the properties described as appertaining to catechine, catechuic, or tanningenic acids, namely, a white substance with a light tint of reddish-brown, a glistening or micaceous aspect when diffused in water, meagre to the feel, something like alumina, insolubility in cold water, and ready solubility, to a great extent, in hot water; forming a brown solution of greater or less intensity in proportion to the quantity dissolved; readily soluble in alcohol and æther, and in the weakest alkaline solutions, without the assistance of heat, forming brown compounds; and with the assistance of heat becoming dark brown, or almost black, owing, it is said, to the absorption of oxygen from the atmosphere, and its conversion into what is called japonic acid, fusible *per se* into a resinous looking substance by the cautious application of heat, and if heated much beyond its fusing point becoming charred, leaving a very bulky charcoal.

If it be considered desirable to undertake the organic ana-

lysis of this substance, in all probability the specimen presented may require further purification, and by adopting the process recommended by Svanberg, namely, forming it into a catechuate of lead, and decomposing this by sulphuretted hydrogen while warm, may in the hands of others be effectual for the purpose, but I confess it has not succeeded well with me.

Catechu.

12·3	Water.
62·8	Tannin.
8·2	Extractive or colouring matter.
2·	Resinous matter.
8·5	Mucilaginous or gummy matter.
4·4	Insoluble matter.
98·2	

Cutch.

12·8	Water.
47·7	Tannin { 41·5 tannin. 6·2 altered tannin.
9·2	Extractive or colouring matter.
13·6	Mucilaginous or gummy matter.
6·8	Resinous matter.
9·4	Insoluble matter.
99·5	

XCIII. *On a curious Change in the Molecular Structure of Silver.* *By* Robert Warington, *Esq.*

THE subject of the present brief communication was put into my hands by my friend Mr. Porrett after our last Meeting, as bearing on the subject of the memoir which I had the honour of reading before the Society in January 1842*; a subject I am still prosecuting, as my time will permit, and the results of which I hope to lay before the Society at an early date.

It appears, from information furnished me by Mr. Porrett, to have been part of a silver funeral vase, and was discovered by some labourers, about four months since, at the depth of seven feet below the surface of the ground, while digging for brick-earth between Bow and Stratford. Its height was about ten inches, and its greatest diameter about eight inches; it weighed 40 ounces, and had a smaller vase about the size of a human heart in its interior. When brought to Mr. Edwards, a watchmaker resident in Shoreditch, by whom it was purchased, it was without a cover, and the contents had been thrown away, with the exception of some black ashes, which

* See Memoirs, vol. i. p. 77.

were not preserved. Its thickness was about from 0·015 to 0·017 of an inch, its surface presented a dull tarnished aspect, and was stained in patches with red oxide of iron. It was extremely rotten and brittle, breaking by the application of the slightest force; the surfaces of fracture were uneven and of a bright white metallic lustre. When examined under the microscope by a power magnifying 100 diameters it presented a highly crystalline structure, the facets of the crystals being exceedingly bright and approaching the cubic form, but none of them could be observed perfectly developed; they were more analogous to the characters of grain tin in its broken state as met with in commerce. It appeared also as though there had been a recrystallization of the metal, as the particles looked as if they had been drawn from the central part to the sides of the thin plate, leaving cavities or interstices of considerable extent and depth; the exterior surface was also coated with a film of about 0·0005 of an inch thick, having a grayish-olive colour, and totally different in its structure from the other parts, being striated across its breadth. The specific gravity of the metal in this state was found to be 9·937, great care having been taken to remove the air from the internal cavities by means of the air-pump.

The metal was next heated to redness in a crucible, and the heat sustained for about ten minutes, after which its characters were found to be totally altered; it had lost its extreme brittleness, requiring to be bent several times before a fracture could be effected, and then, by the aid of the microscope, exhibited a close, small grained tough aspect of a dull white colour, and without the previous cavernous appearances; the superficial film seemed also in places to have partially separated from the substance of the thin plate of metal during the bending. The specific gravity was again taken, adopting the previous precautions, and was found to be 9·95, making an increase of 0·013 on the gravity taken before the application of a red heat.

It was next submitted to analysis; 8·5 grains were digested in dilute nitric acid, and the soluble parts (A) decanted, and the residue well washed. This residue was in small thin grayish-white flakes, and by exposure to the light became rapidly of a purple tint, indicating the presence of chloride of silver; fearing that this might have arisen from some accidental impurity in the materials employed, both the nitric acid and distilled water were carefully tested and proved to be perfectly pure; it was therefore digested in weak solution of ammonia, which dissolved the whole, with the exception of a small quantity of brown powder, which was found to consist

of 0·06 gr. of peroxide of iron and a trace of gold. The ammoniacal solution was precipitated by nitric acid, and gave 0·52 gr. of chloride of silver. The solution (A) was next precipitated by solution of chloride of sodium, and gave 10·25 grains of chloride of silver, equivalent to 7·66 grains of silver; solution of caustic potash, and boiling threw down the oxide of copper, and yielded 0·30 gr. oxide of copper = 0·24 gr. of copper. Thus we have—

Silver	7·66 grains.
Chloride of silver. . .	0·52 ...
Copper	0·24 ...
Oxide of iron	0·06 ...
Gold	a trace
	8·48
Loss .	0·02
	8·50

It becomes a curious question as to the origin of this chloride of silver, which was evidently the superficial grayish film observed under the microscope, and which partially separated in the act of bending the metal after heating. That it must have been produced by the continued action of chlorides, perhaps aided by sulphates present in the brick clay from which the vase was excavated, there can be little doubt, and the peroxide of iron also existing in the clay may have assisted this action.

The passage of the metal to the brittle state in this and in all other cases will, I think, be found attributable to some electrical action arising from sudden cooling, vibration or concussion, chemical action, &c. to which the metallic body or alloy may have been exposed.

January 1, 1844.—The President in the Chair.

Mr. Warington presented Specimens of Chloride of Antimony and of Bichloride of Mercury in Crystals to the Society's Museum.

William Lucas, Esq., James P. Joule, Esq., and Charles J. Hodgson, Esq., were elected Members.

The following communications were then read:—

On the Heat disengaged in Combinations. By Thomas Graham, *Esq., F.R.S., &c.* (*Was commenced.*)

XCIV. *On a Class of Double Sulphates, containing Soda and a Magnesian Oxide. By* A. R. Arrott, *Esq.*

WHEN a mixed solution of sulphate of soda and any of the magnesian sulphates is allowed to crystallize by spontaneous evaporation, these salts always separate from their

solution apart and in their ordinary form, no double salt being produced.

I find however that if the solution be kept at a temperature exceeding 100° F., the temperature at which anhydrous sulphate of soda begins to be deposited, a double salt is formed, and this is true of all the magnesian sulphates. The double salts may generally be procured in well-defined crystals, except that of copper, which is usually deposited as a crystalline crust.

One member of this class of double sulphates, namely the sulphate of magnesia and soda, was obtained by Dr. Murray in the manufacture of sulphate of magnesia from sea water, being produced accidentally during the evaporation of the liquor; but he seems not to have been aware of the circumstances of its formation.

Several soda salts of the same class were also obtained by Mr. Graham by a process which he has described, namely, by mixing strong solutions of bisulphate of soda and the magnesian sulphate in atomic proportions; the double salt separated by crystallization in the course of a few days, at the ordinary temperature. The reason why no double salt of soda is formed at low temperatures seems to be the affinity of sulphate of soda for water, and the consequent formation of a hydrated sulphate of that base, which cannot enter into such combinations.

This interference is, however, prevented by the use of a high temperature, at which, as is well known, sulphate of soda is deposited from its solution in the anhydrous condition, and probably therefore exists dissolved in that state.

The method which succeeds best is to dissolve the salts together in equivalent quantities, and to evaporate at a temperature of 130°. In this way I have formed the double salts of soda with magnesia, zinc, iron, copper and manganese.

The quantity of water contained in 100 parts of these salts was—

	Experiment.	Theory.	
Sulphate of magnesia and soda	21·68	21·38	4 HO
... zinc ...	19·76	19·15	4 HO
... iron ...	19·86	19·69	4 HO
... copper ...	11·00	10·63	2 HO
... manganese	11·09	10·89	2 HO

which gives 4 atoms in the magnesia, zinc and iron salts, and 2 in those of manganese and copper, the per-centage of water observed being in all cases rather above the atomic quantity, from water mechanically included; double salts being, as is

well known, remarkable for the quantity of hygrometric water they retain.

The salt of magnesia is generally said, on the authority of Dr. Murray, to contain 6 atoms of water, but I have never found it to contain more than 4.

These salts are persistent in air, and may be dried at 212° without losing their transparency; the salts of manganese and magnesia decrepitate strongly when heated.

After the loss of their water, these salts are all fusible at a low red heat, and undergo that change without decomposition.

When the double salt is dissolved in water and the solution allowed to evaporate spontaneously, its component salts always crystallize apart, the double salt being entirely decomposed; this often happens also with bisulphate of soda. In consequence of this effect of water the solubility at a low temperature could not be observed.

When a solution of the copper salt is boiled, a subsalt is precipitated, resembling the subsalt of copper and potash formed under similar circumstances. It is of a pale green colour, loses nothing by drying at 212°, but loses weight and becomes much deeper in colour when ignited; it therefore contains water besides an excess of oxide of copper.

January 15, 1844.—The President in the Chair.

The following presents were announced since the last Meeting:—

"Lessons on Chemistry," by W. H. Balmain, from the author.

"Two Lectures on the application of Physiology in Rearing and Feeding Cattle," by Lyon Playfair, Ph.D., from the author.

Douglas Maclagan, M.D., and G. E. Day, M.D., were elected Members of the Society; and Mr. John Thom an Associate.

The following communications were then read:—

XCV. *Experiments on the Heat disengaged in Combinations.* *By* Thomas Graham, *Esq.*, *F.R.S.*, *&c.* (*Was resumed.*)

Part II. *Neutralization of various Acids by Hydrate of Potash.*

THE arrangements adopted for observing the heat evolved on neutralizing acids by potash were similar to those described in the former paper. The same platinum crucible, weighing 1201·9 grains, and hollow cylinder of palladium, weighing 207·6 grains, were employed as the containing vessel and stirrer; but the constant quantity of water employed as a vehicle for the acid and alkali was increased from 1000 grains to 1544 grains, or 100 grammes, while the equivalent quantities of the substances used were the same as before. The solution of the saline body formed in an experiment was consequently one-half more dilute, and the small but sensible

effect of further dilution of the solution in producing cold, observable in some of the former experiments, was thus entirely avoided, while the increase of the mass of fluid reduced the influence of external causes on its temperature. A mercurial thermometer of greater delicacy was employed, of which the bulb was a cylinder of 1·25 inch in length and 0·3 inch in diameter; the scale was graduated into degrees Fahrenheit, ranging from 40° to 70°, each degree being 0·42 inch in length (0·74 inch for one degree centigrade), divided into tenths of a degree, each of which could again be subdivided into fifths by the eye, so that the observation was made to one-fiftieth of a degree Fahrenheit. The eye was directed to the scale through a straight cylindrical tube of small diameter, supported in a horizontal position. The mercury in the bulb of the thermometer was equivalent in capacity for heat to 11·5 grains of water, and the containing vessel and stirrer to 49 grains, making together 60·5 grains of water; the capacity of the salt dissolved or formed rarely exceeded that of 12 grains of water.

I. *Neutralization of Hydrate of Potash by Nitric and Hydrochloric Acids.*

The equivalent proportion of this acid adopted in these experiments is 33·85 grains, that is one-twentieth of 677, the usual equivalent of nitric acid on the oxygen scale. Nearly one-half the quantity mentioned was used in an experiment, namely 0·455 equivalent, diluted in the crucible with about four-fifths of the water, while the remaining portion of the 1544 grains of water, in a small and thin glass flask, contained hydrate of potash in quantity sufficient to saturate the acid, and leave a *slight* excess of alkali. The two liquids were afterwards brought to exactly the same temperature, which was observed by two thermometers, the corresponding points of which were accurately determined, and the potash solution then emptied into the nitric acid. The following are the results of three observations of the temperature of the liquids before mixture, and the temperature after mixture:—

Before mixture . .	61°·91	62°·13	62°·13
After mixture . . .	66°·70	66°·91	66°·89
Rise of temperature .	4°·79	4°·78	4°·76

Increasing 4°·78 the mean of the experiments, in the proportion of 0·455 to 1, we have 10°·50 as the rise of temperature on saturating a whole equivalent of potash by nitric acid.

The heat evolved upon combination is sensibly affected by a considerable difference in the temperatures at which the acid and alkali are mixed; being less at the lower temperature.

This appears by the following experiments, in which 0·5 equivalent of nitric acid was neutralized at a temperature twenty-two degrees lower than in the former experiments.

Before mixture . .	40°·25	40°·60	
After mixture . . .	45°·43	45°·80	
Rise of temperature .	5°·18	5°·20	Mean 5°·19.

Hence we have the heat from the neutralization of nitric acid by hydrate of potash—

10°·50, at 62° F.
10°·38, at 40° F.

Half an equivalent of hydrochloric acid, 11·38 grains, was neutralized with hydrate of potash in slight excess, exactly as the nitric acid was treated in the preceding experiment.

Before mixture . .	60°·20	60°·00	59°·95
After mixture . . .	65°·30	65°·15	65°·10
Rise of temperature .	5°·10	5°·15	5°·15

Mean rise 5°·13 for 0·5 equivalent of hydrochloric acid, or 10°·26 for 1 equivalent of that acid. The neutralization of hydrate of potash, therefore, in very dilute solutions with these two different acids produces nearly the same disengagement of heat, the result with nitric acid being 10°·50.

The heat of combination appears also to be sensibly affected in amount by the temperature of the experiment:—

Before mixture . .	40°·00	40°·25	
After mixture . . .	45°·02	45°·30	
Rise of temperature .	5°·02	5°·05	Mean 5°·03

From which it follows that the heat from the neutralization of hydrochloric acid by hydrate of potash is—

10°·26, at 60° F.
10°·06, at 40° F.

It is remarkable how large a proportion the cold produced on dissolving in water crystallized nitrate of potash and chloride of potassium, the salts produced in these experiments, bears to the heat observed in the formation of the same salts.

One equivalent of crystallized nitrate of potash (63·25 grs.) well dried, pounded and sifted, was dissolved in the usual quantity of water:—

Before solution .	61°·80	62°·20	61°·88	
After solution . .	56°·10	56°·45	56°·18	
Fall of temperature	5°·70	5°·75	5°·70	Mean 5°·72.
Before solution .	56 ·45	57°·70	55°·45	
After solution . .	50°·80	52°·00	49°·75	
Fall of temperature	5°·65	5°·70	5°·70	Mean 5°·68.

The cold on dissolving this salt is not quite constant, but increases sensibly at low temperatures, a law which appears to prevail in a class of salts:—

Before solution .	47°·00	46°·40	45°·95	
After solution . .	41°·05	40°·47	40°·00	
Fall of temperature	5°·95	5°·93	5°·95	Mean 5°·94.

It appears, on comparing the last set of experiments with that immediately preceding it, that a difference of ten degrees at this part of the scale makes a difference of 0°·26, or 1-22nd part, in the fall of temperature consequent upon the solution of an equivalent of nitrate of potash. It is this increased absorption of heat at the low temperature probably which occasions the observed heat of combination of the salt to diminish at the same part of the scale.

On the other hand, the cold, on dissolving several equivalents of nitrate of potash successively at a constant temperature, in the same quantity of water diminishes considerably with the number of equivalents of salt dissolved. The capacity for heat of the crystallized salt is 0·239 (Regnault).

Dissolved in 1544 grains of water,

First equivalent of nitrate of potash:—

	62°·34	63°·68	
	56°·68	57°·90	
Fall	5°·66	5°·78	Mean 5°·72.

Second equivalent of nitrate of potash:—

	63°·47	63°·12	
	58°·17	57°·86	
Fall	5°·30	5°·26	Mean 5°·28.

Third equivalent of nitrate of potash:—

	63°·40	63°·56	
	58°·47	58°·61	
Fall	4°·93	4°·95	Mean 4°·94.

Fourth equivalent of nitrate of potash:—

	63°·57	63°·35	
	58°·95	58°·76	
Fall	4°·62	4°·59	

Fifth equivalent of nitrate of potash:—

	63°·40	63°·34	
	59°·08	59°·10	
Fall	4°·32	4°·24	Mean 4°·28.

Sixth equivalent of nitrate of potash:—

	63°·45
	69°·63
Fall	3°·82

In consequence of this diminished absorption of heat in the solution of the latter equivalents of nitrate of potash, the addition of water to the strong solution finally obtained occasions a further absorption of heat; or dilution produces cold.

The last prepared solution, which consisted of 379·5 grains of nitrate of potash dissolved in 1544 grains of water, and is a solution nearly saturated for the temperature, was mixed with another 1544 grains of water in a pint silver crucible with silver spatula, weighing 1650 grains, both liquids being at the same temperature:—

Before mixture . .	63°·19
After mixture . . .	61°·91
Fall of temperature .	1°·28

A second portion of 1544 grains of water being added to the above solution, occasioned a further fall of temperature:—

Before mixture . .	63°·57
After mixture . . .	63°·19
Fall	0°·38

It appears from these experiments on the solution of successive equivalents of nitrate of potash in the same quantity of water, that much of the cold on dissolving that salt is properly referable to the dilution of the solution, and not to the simple liquefaction or solution of the crystalline salt. But this is more obvious in dissolving a salt of great solubility, such as nitrate of ammonia, of which many more equivalents may be dissolved in succession.

Dissolved in 1544 grains of water,

100·4 grains, or 2 equivalents of nitrate of ammonia:—

	66°·25
	57°·91
Fall	8°·34

Third and fourth equivalents:—

	66°·43
	58°·91
Fall	7°·52

Fifth and sixth equivalents:—

	66°·21
	59°·36
Fall	6°·85

Seventh and eighth equivalents:—

	66°·10
	59°·82
Fall	6°·28

Ninth and tenth equivalents:—

	66°·26
	60°·41
Fall	5°·85

Eleventh and twelfth equivalents:—

66°·53
61°·06
Fall 5°·47

Thirteenth and fourteenth equivalents:—

66°·45
61°·29
Fall 5°·16

Fifteenth and sixteenth equivalents:—

66°·47
61°·55
Fall 4°·92

Seventeenth and eighteenth equivalents:—

66°·61
61°·99
Fall 4°·62

Nineteenth and twentieth equivalents:—

66°·26
61°·91
Fall 4°·35

Twenty-first and twenty-second equivalents:—

66°·58
62°·45
Fall 4°·13

Twenty-third and twenty-fourth equivalents:—

66°·66
62°·63
Fall 4°·03

Twenty-fifth and twenty-sixth equivalents:—

66°·83
63°·16
Fall 3°·67

Twenty-seventh and twenty-eighth equivalents:—

66°·53
62°·97
Fall 3°·56

Twenty-ninth and thirtieth equivalents:—

66°·57
63°·24
Fall 3°·33

Thirty-first and thirty-second equivalents:—

66°·80
63°·57
Fall 3°·23

Thirty-third and thirty-fourth equivalents:—

66°·37
63°·24
Fall 3°·13

Thirty-fifth and thirty-sixth equivalents:—

66°·45
63°·50
Fall 2°·95

Here we find that while the fall on the solution of the first two equivalents of nitrate of ammonia is 8°·34, that of the last two dissolved is only 2°·95, or little more than a third of the former. The liquid, however, finally consisted of 1544 grains of water and 1807·2 grains of salt, and would therefore have a considerably greater capacity for heat than the water alone; but the proper correction for this increase of capacity cannot at present be made, as the specific heat of nitrate of ammonia has not been ascertained.

The last solution of nitrate of ammonia, which was nearly saturated for the temperature, was of density 1°·247. Three portions of 100 grammes of water were added to it in succession, to discover the cold produced on dilution.

First 100 grammes of water:—	
Before mixture . .	66°·83
After mixture . . .	60°·27
Fall	6°·56
Second 100 grammes of water:—	
Before mixture . .	67°·06
After mixture . . .	64°·40
Fall	2°·66
Third 100 grammes of water:—	
Before mixture . .	67°·06
After mixture . . .	65°·61
Fall	1°·45

The high solubility of the nitrate of soda adapts it for similar experiments. It will be observed that a difference of 13 degrees of temperature does not materially affect the amount of heat absorbed on dissolving a single equivalent of this salt. The capacity for heat of the crystallized salt is 0·278 (Regnault).

One equivalent of nitrate of soda, 53·40 grains, dissolved in 100 grammes of water:—

Before solution . .	65°·07	51°·78	51°·63
After solution . . .	61°·56	48°·25	48°·08
Fall	3°·51	3°·53	3°·55

Ten equivalents of this salt being dissolved successively in the same 100 grammes of water, the following changes of temperature were observed:—

	I.	II.	III.	IV.	V.
	65°·07	65°·01	64°·63	64°·80	64°·84
	61°·56	61°·70	61°·65	63°·14	62°·29
Fall .	3°·51	3°·31	2°·98	2°·66	2°·55
	VI.	VII.	VIII.	IX.	X.
	64°·77	64°·63	64°·89	64°·77	64°·64
	62°·38	62°·34	62°·74	62°·79	62°·76
Fall .	2°·39	2°·29	2°·15	1°·98	1°·88

The solution of the tenth equivalent of this salt produces therefore only one-half the cold due to the first equivalent.

The solution of chloride of potassium in water is attended with a fall of temperature, which is considerable, although not so great as with nitrate of potash.

One equivalent of chloride of potassium (46·62 grains) dissolved in 100 grammes of water:—

Before solution . .	62°·05	61°·80	61°·70	
After solution . . .	59°·10	58°·88	58°·75	
Fall of temperature .	2°·95	2°·92	2°·95	Mean 2°·94.

At a lower temperature:—

Before solution . .	45°·55	45°·04	45°·53	
After solution . . .	42°·55	42°·02	42°·50	
Fall of temperature .	3°·00	3°·02	3°·03	Mean 3°·02.

II. *Neutralization of Hydrate of Potash by Sulphuric Acid.*

Half an equivalent of sulphuric acid, 12·53 grains, was saturated with a slight excess of hydrate of potash, the united liquids containing 100 grammes of water, as in the preceding experiments with nitric and hydrochloric acids:—

Before mixture . .	61°·31	61°·45	61°·53	
After mixture . . .	67°·01	67°·13	67°·21	
Rise	5°·70	5°·68	5°·68	Mean 5°·69.

The rise of temperature on saturating a whole equivalent of hydrate of potash with sulphuric acid will therefore be 11°·38.

The saturation of sulphate of water, already in combination with sulphate of potash in the bisulphate of that base, is attended with the disengagement of a still greater quantity of heat. Half an equivalent of fused bisulphate of potash, dissolved in water like the acid of the former experiments, was neutralized by potash, with the usual conditions:—

Before mixture . .	62°·74	62°·92	63°·05	
After mixture . . .	68°·95	69°·12	69°·22	
Rise	6°·21	6°·20	6°·17	Mean 6°·19.

The saturation of the whole equivalent of sulphate of water in a solution of the bisulphate of potash therefore occasions the disengagement of 12°·38; free sulphate of water only 11°·38; the excess in the former case being 1°·00.

Now, in saturating two equivalents of sulphuric acid, the heat evolved is twice 11°·38, or 22°·76; but as 12°·38 is evolved in saturating the second equivalent of sulphuric acid, it follows that 10°·38 only are evolved in saturating the first equivalent of acid. Hence we have—

Heat disengaged in the formation of bisulphate of potash	10°·38
... ... saturating acid of	12°·38
	22°·76

The cold, on dissolving an equivalent of crystallized sul-

phate of potash, 54·55 grains, in 100 grammes of water, was also observed :—

Before solution . .	66°·69	66°·01	66°·27	
After solution . . .	64°·38	63°·75	63°·96	
Fall	2°·31	2°·26	2°·31	Mean 2°·29.

On mixing solutions of sulphate of potash and sulphate of water (dilute sulphuric acid), to form bisulphate of potash, cold is produced, as was formerly observed; and from this cause sulphate of potash, when dissolved in water acidulated with sulphuric acid, produces more cold than in pure water, by about one-third of the quantity from the latter. This excess of heat absorbed I was disposed to connect with the combination of sulphate of water with sulphate of potash, and formation of a double salt. But it is remarkable that the magnesian sulphates, which we do not certainly know to combine with hydrated acids, as sulphate of potash does, likewise produce greater cold on dissolving in acidulated than in pure water.

Thus an equivalent of crystallized sulphate of magnesia, which dissolves in 1000 grains of water with a fall of 0°·88 R. (Chemical Memoirs, vol. i. p. 111), dissolved in the same quantity of water already containing an equivalent of sulphuric acid with a fall of 1°·12, 1°·17, 1°·18 R. in three experiments; of which the mean is 1°·16, being 0°·28 more than in pure water. A second equivalent of crystallized sulphate of magnesia, when dissolved in the same liquor, produced a fall, in three experiments, of 0°·96, 0°·92, 0°·95 R., of which the mean is 0°·94, or only 0°·06 more than in pure water.

In an equivalent of nitric or of hydrochloric acid, the fall from the solution of an equivalent of crystallized sulphate of magnesia was nearly double what it is in pure water.

The fall in water containing 1 equivalent of nitric acid was 1°·70, 1°·68, 1°·64, of which the mean is 1°·67.

The fall in water containing 1 equivalent of hydrochloric acid was 1°·70, 1°·70, 1°·68; mean 1°·69 R.

The fall on the solution of 1 equivalent of sulphate of magnesia in ½ equivalent of hydrochloric acid was 1°·37, 1°·37, 1°·38; mean 1°·37 R. The excess of cold produced by the half equivalent of this acid, over water alone, was therefore 0°·50; the excess by the whole equivalent of acid 0°·82; so that fully more than one-half of the effect is produced by the first half equivalent of acid.

An excess above 1 equivalent of acid to 1 equivalent of a salt of this class increases the depression of temperature still further, but in a less degree than the direct proportion of its

quantity. Thus the cold on dissolving 1 equivalent of sulphate of zinc in water being 1°·02 R.,—

In $1\frac{1}{2}$ equivalent of sulphuric acid, 1°·22, 1°·19, 1°·25; mean 1°·22.

In 1 equivalent of nitric acid, 1°·56, 1°·55, 1°·54; mean 1°·55.

In $\frac{1}{2}$ equivalent of hydrochloric acid, 1°·50, 1°·50, 1°·47; mean 1°·49.

In 1 equivalent of hydrochloric acid, 1°·82, 1°83, 1°·86; mean 1°·83.

In 2 equivalents of hydrochloric acid, 2°·26, 2°·26, 2°·24; mean 2°·25.

The solution of an equivalent of crystallized sulphate of iron was attended with a fall of temperature,—

In water of 1°·06 R.

In 1 equivalent of sulphuric acid, of 1°·28, 1°·20, 1°·26, 1°·25; mean 1°·25.

In 1 equivalent of hydrochloric acid, of 1°·69, 1°·68, 1°·73; mean 1·°70.

The solution of an equivalent of crystallized sulphate of copper was attended with a fall of temperature,—

In water of 0°·63 R.

In 1 equivalent of sulphuric acid, of 0°·94, 0°·96, 1°·02; mean 0°·97 R.

The mixture of an equivalent of *sulphate of water*, 30·68 grains, in 300 grains of water, with another 700 grains of water, occasioned a rise of 0°·09 R.; with 700 grains of water containing 1 equivalent of hydrochloric acid a rise of 0°·16, and with 700 grains of water containing 1 equivalent of nitric acid, 0°·00.

The magnesian sulphates generally resemble sulphate of water in producing heat and not cold on dilution of their strong solutions. The solutions of the three following salts were saturated in the cold:—

Sulphate of zinc (density 1·395), with equal bulk of water, +0°·60.

Sulphate of magnesia (density 1·294), with equal bulk of water, +0°·60.

Protosulphate of iron (density 1·227), with equal bulk of water, +0°·04.

The experiments on the solution of salts in acids leave it doubtful, whether the additional depression of temperature is due in every case and entirely to a combination of the salt with the acid, as it may be supposed to be when sulphate of potash is dissolved in dilute sulphuric acid, bisulphate of potash being then formed, or whether it is a consequence of a

partial decomposition of the salt by the free acid to which it is exposed. The small portion of acid, generally a single equivalent, which produces the greatest proportional effect, seems to indicate that combination or decomposition is the cause, rather than any alteration in the solvent power of the liquid. The action of hydrochloric acid and of nitric acid is often the same, and is greater than that of sulphuric acid. This appears even in the solution of a magnesian chloride in water and in these acids.

Thus 42·29 grains, 1 equivalent, of the fused anhydrous chloride of zinc were dissolved in 1000 grains of water with a rise in two experiments of 3°·42, 3°·45 R., of which the mean is 3°·44 R. In 1000 grains of water containing 1 equivalent of sulphuric acid, with a rise of 3°·43, 3°·42, 3°·42 R., in three experiments; which is nearly the same result as in pure water. In the same quantity of water containing 1 equivalent of hydrochloric acid, with a rise of 2°·86, 2°·88, 2°·86; of which the mean is 2°·87 R., being 0°·57 less heat than in water alone. The presence of the hydrochloric acid has therefore occasioned a fall of 0°·57 in the solution of chloride of zinc, while the action of sulphuric acid is insensible.

An alkaline chloride was little affected by the presence of an equivalent of these acids in the water in which it was dissolved. Thus *chloride of sodium* was dissolved with a fall—

In 1000 grs. water,		of 0°·57, 0°·60,	Mean 0°·59 R.
...	+ HCl,	of 0°·60, 0°·60, 0°·60,	... 0°·60 R.
...	+ NO_5,	of 0°·50, 0°·50, 0°·52,	... 0°·51 R.
...	+ SO_3,	of 0°·50, 0°·50, 0°·43,	... 0°·48 R.

To obtain light upon this influence of acids on the thermal phænomena of the solution of salts, experiments were made upon two other salts. *Sulphate of ammonia* without any water of crystallization (1 equivalent, or 41·41 grains) was observed to dissolve in 1000 grains of water with a fall of 0°·51 R. In water containing $\frac{1}{2}$ HCl, with a fall of 1°·12, 1°·10, and 1°·12 R.; mean 1°·11. In water containing HCl, with a fall of 1°·30, 1°·22, 1°·28; mean 1°·27 R. In water containing NO_5, with a fall of 1°·28, 1°·30, 1°·30; mean 1°·29 R. In water containing SO_3, with a fall of 0°·92, 0°·92, 0°·90; mean 0°·92 R. The addition of a second equivalent of highly diluted sulphuric acid to the last solution produced a change of temperature in three experiments of 0°·02, 0°·00, 0°·00. The addition of a second equivalent of sulphate of ammonia to the preceding solutions of the bisulphate of ammonia, occasioned a fall of 0°·58, 0°·55, 0°·60 R.; mean 0°·58, or very little more than in pure water

(0°·51). In 1544 grains of water containing 1 equivalent of acetic acid (32·15 grains), with a fall of 0°·84, 0°·78, 0°·81 F., of which the mean is 0°·81 F., the experiment being made at 67° F. In 1 equivalent of oxalic acid (22·64 grains), with a fall of 1°·20, 1°·21 and 1°·22 F., the experiment being made at 65° F. To render the last two experiments comparable with the former, they must be reduced in the proportion of 19 to 13, that is, the effect of the acetic acid to 0°·55 R., of the oxalic acid to 0°·83 R.; so that the influence of the acetic acid is almost nothing, of the oxalic acid much less than that of the mineral acids.

While 1 equivalent of *nitrate of potash* was dissolved in 1000 grains of water at 63° F., with a fall of 3°·76, 3°·72 and 3°·80 R., of which the mean is 3°·76; it was dissolved in the same quantity of water containing 1 equivalent of nitric acid at 67° F., with a fall of 3°·64, 3°·54, 3°·64 R., of which the mean is 3°·57; in the same quantity of water containing 1 equivalent of sulphuric acid at 58° F., with a fall of 3°·53, 3°·50, 3°·50 R., of which the mean is 3°·51.

The mere mixing of solutions of such neutral salts as are understood to combine together and form a double salt, is not attended with such changes of temperature. No sensible change of temperature was perceived on mixing dilute solutions of a magnesian and potash sulphate; and one of these salts was dissolved in a solution of the other with the same fall of temperature as in pure water. Although I think it all but certain that these salts combine at once on mixing, I could not discover a single circumstance which was decisive of the fact. The density of such a mixture of salts was not altered by boiling it alone or with spongy platinum, and was exactly the same as that of the liquid formed on dissolving in water a corresponding quantity of the crystallized double sulphate. The addition of an equivalent of sulphuric acid already highly diluted to each of the solutions thus compared, produced exactly the same fall of temperature. On the other hand, this fall of temperature was as nearly as possible the same as that obtained on dividing the acid into two equal portions, and mixing separately a solution of each of the constituent salts with each portion. The solution of a double salt appears therefore to be as nearly as possible equivalent to the constituent salts dissolved apart. Even in the formation of *alum* no certain change of temperature was observable; one-fourth of an equivalent of sulphate of potash (13·63 grains), when dissolved in 1000 grains of water, producing a fall of 0°·32 R., while when dissolved in 1000 grains of water containing one-fourth of $Al_2 O_3 + 3 SO_3$, the fall was 0°·35, 0°32, 0°35 R.,

of which the mean is 0°·34; the experiments being made at 57° F.

But these double sulphates being all less soluble than their constituent sulphates, it was desirable to make the experiment upon the formation of a double salt, which is more soluble than its constituents; such as the double chloride of mercury and ammonium. One-half of an equivalent of chloride of mercury, 42·70 grains, was dissolved in 1544 grains of water at 64° F., with a fall of 0°·29, 0°·30, 0°·30 F., of which the mean is 0°·30 F. The same quantity of chloride of mercury was dissolved in 1544 grains of water, containing half an equivalent, 16·74 grains, of chloride of ammonium, at 63° F., with a fall of 0°·13, 0°·12, 0°·12 F., of which the mean is 0°·12 F. Doubling these results, we have the fall from a whole equivalent of chloride of mercury in water equal to 0°·60; from chloride of mercury in chloride of ammonium 0°·24; the difference, or 0°·36, being due to heat evolved in the formation of the double salt. The latter, however, or sal-alembroth, assumes an atom of water of crystallization in its formation, which may perhaps occasion some change of temperature.

When 1 equivalent of chloride of mercury was dissolved in half an equivalent of chloride of ammonium at 63°, the fall was 0°·45, 0°·45, 0°·47 F., of which the mean is 0°·46 F. The disengagement of heat in the formation of this second double salt is therefore $0°{\cdot}60 - 0°{\cdot}46 = 0°{\cdot}14$ F. It is doubtful whether the heat here can be ascribed to hydration; as the resulting double salt has been crystallized at the usual temperature by Dr. Kane, both anhydrous and with one atom of water. The circumstance however of the chloride of mercury being dissolved by a solution of sal-ammoniac in much larger quantity than by pure water, affords a proof of the immediate formation of a double salt on the solution of its constituents together, which cannot be obtained in the magnesian or aluminous double sulphates.

I may be allowed to place under the present head of sulphuric acid, the results of experiments on the solution in water of two double sulphates, namely sulphate of zinc and soda, and sulphate of manganese and soda, no experiment on a double salt of the soda division of this class being recorded in the former paper. The *sulphate of zinc and soda*, formed by Mr. Arrott, was in excellent crystals, containing four atoms of water; of which the composition is expressed by the formula $ZnO, SO_3 + NaO, SO_3 + 4\,HO$. One-half of an equivalent, 58·61 grains of the salt, containing 11·25 grains of water of crystallization, was dissolved in 988·8 grains of water

at 62° F., with a fall in three experiments of 0°·02 R., 0°·04, 0°·02; mean 0°·03 R.

Of the same salt made anhydrous by heat and fused, half an equivalent, or 47·41 grains, was dissolved in 1000 grains of water at 62° F., with a rise in three experiments of 1°·86, 1°·87, 1°·84; mean 1°·86 R. Doubling the results of the experiments in both cases, to obtain the changes for a whole equivalent, we find—

Cold on solution of $ZnO, SO_3 + NaO, SO_3 + 4\,HO$ 0°·06 R.
Heat on solution of $ZnO, SO_3 + NaO, SO_3$ 3°·72 R.

As the two sulphates, in all the double sulphates of this class containing sulphate of soda, crystallize apart when the salt is dissolved in water at 62°, the double salt is probably decomposed in these experiments; and the circumstances of its solution may therefore be very different from those of a magnesian double sulphate containing sulphate of potash.

The *sulphate of manganese and soda*, for which I am also indebted to Mr Arrott, was in good crystals containing two atoms of water; the formula of this salt being $MnO, SO_3 + NaO, SO_3 + 2\,HO$. 1 equivalent of the crystallized salt, 103·2 grains, containing 11·25 grains of water of crystallization, was dissolved in 988·8 grains of water, with a rise of temperature in three experiments of 0°·77, 0°·70, and 0°·70; of which the mean is 0°·72 R.

Of the same salt, fused by heat and anhydrous, 1 equivalent, 91·95 grains, was dissolved in 1000 grains of water, with a rise in two experiments of 3°·02 and 2°·99; of which the mean is 3°·00 R. The results, therefore, for this double salt, are—

Heat on solution of $MnO, SO_3 + 2\,HO$. 0°·72
... ... MnO, SO_3 . . . . 3°·00

III. *Neutralization of Bichromate of Potash by Hydrate of Potash.*

Half an equivalent of bichromate of potash, 47·34 grains, and a little more than half an equivalent of hydrate of potash contained separately in different portions of the usual quantity 1544 grains or 100 grammes of water, were brought to the same temperatures exactly, and mixed in two experiments:—

Before mixture . .	63°·23	63°·50
After mixture . . .	67°·71	67°·97
Rise of temperature .	4°·48	4°·47

Doubling 4°·48, the mean result, we have 8°·96 F. as the heat evolved on neutralizing the second equivalent of chromic acid in bichromate of potash.

Of the neutral or yellow chromate of potash, which is the product of this neutralization, 1 equivalent, 62·08 grains, was dissolved by 1544 grains of water at 65° F., with a fall in three experiments of 1°·82, 1°·81 and 1°·87, of which the mean is 1°·83.

IV. *Neutralization of Acetic Acid by Hydrate of Potash.*

Half an equivalent of acetic acid, 16·08 grains, was neutralized by potash in very slight excess, as in the other experiments:—

Before mixture . .	63°·52	63°·81	63°·94
After mixture . . .	68°·68	68°·98	69°·12
Rise of temperature .	5°·16	5°·17	5°·18

The mean result of these experiments 5°·17 being doubled, we have 10°·34 F. as the heat evolved on the saturation of acetic acid by hydrate of potash.

Of acetate of potash fused without becoming black, 1 equivalent, 61·65 grains, was dissolved in 1544 grains of water at 65° F., with a rise of temperature in three experiments of 2°·45, 2°·47, 2°·44; of which the mean is 2°·45 F.

V. *Neutralization of Oxalic Acid by Hydrate of Potash.*

Half an equivalent of oxalic acid was neutralized by potash under the usual circumstances:—

Before mixture . .	64°·60	64°·66	64°·69
After mixture . . .	69°·84	69°·89	69°·95
Rise of temperature .	5°·24	5°·23	5°·26

Doubling 5°·24, the mean result, we have 10°·48 F. as the heat evolved on the saturation of a whole equivalent of oxalic acid by hydrate of potash.

One equivalent of *crystallized oxalic acid*, 39·50 grains, containing 12·5 grains of water of crystallization, was dissolved in 1533 grains of water at 67° F., with a fall of 3°·04, 3°·06, 3°·04; of which the mean is 3°·05.

One equivalent of *oxalate of water* deprived of its water of crystallization, 28·25 grains, was dissolved in 1544 grains of water at 67° F., with a fall of 0°·99, 0°·99, 1°·01; of which 1°·00 is the mean. The difference between the falls on solution of the hydrated and anhydrous oxalate, is occasioned by the hydration of the latter on solution. The heat disengaged when oxalate of water combines with its two atoms of constitutional water is therefore 3°·05 − 1°·00 = 2°·05 F.

Neutral *oxalate of potash* crystallizes with a single atom of water, which requires a heat of 212° to expel it. 1 equi-

valent of the crystallized salt, 57·76 grains, containing 6·25 grains of water, was dissolved in 1538 grains of water at 67° F., with a fall of 2°·65, 2°·66 and 2°·67; of which the mean is 2°·66 F.

Of the same salt made anhydrous by heat, one-half of an equivalent, 25·75 grains, was dissolved in 1544 grains of water, with a fall of 0°·76, 0°·71, 0°·74; of which the mean is 0°·74. A whole equivalent of the salt would therefore have dissolved with a fall of 1°·58, which is 1°·08 less than the fall from the hydrated salt. The last quantity represents the heat of combination of oxalate of potash with one atom of water of crystallization. It approaches nearly to one-half of the heat disengaged by oxalate of water, in combining with two atoms of water, one-half of 2°·05 being 1°·025; the difference is within the errors of observation.

When hydrated oxalate of potash is dissolved in water containing oxalic acid, the change of temperature is very much the same as in pure water, although in the former case a superoxalate will be formed. One-fourth of an equivalent of oxalate of potash, 14°·44 grains, was dissolved in 1544 grains of water containing in solution one-fourth of an equivalent of hydrated oxalic acid, at 67° F., with a fall of 0°·70, 0°·68, 0°·68; mean 0°·68 F. If it were therefore possible to dissolve a whole equivalent of the salt in a whole equivalent of the acid contained in the quantity of water to which we are restricted, the fall would be four times greater, or 2°·72 F., which is nearly the same as the cold on dissolving crystallized oxalate of potash in water, namely 2°·66. Here again little or no heat is observed in forming a double salt, for the binoxalate of potash must be regarded as such.

Binoxalate of Potash. $KO, C_2O_3 + HO, C_2O_3, 2\,HO$.—As with bisulphate of potash, the saturation of the excess of acid in this salt causes the disengagement of more heat than the saturation of the same quantity of free acid. One-fourth of an equivalent of the crystallized binoxalate, 22·91 grains, was neutralized by hydrate of potash at 67°:—

Before mixture . .	66°·80	66°·85	66°·96	
After mixture . . .	69°·91	69°·96	70°·04	
Rise of temperature .	3°·11	3°·11	3°·08	Mean 3°·10

The mean quantity, multiplied by four, gives 12°·40 F., as the heat evolved on neutralizing by potash the second equivalent of oxalic acid in binoxalate of potash. Now distributing the heat from the saturation of two equivalents of oxalic acid, 20°·68 (= 10°·34 × 2), as was done in sulphuric acid, we have—

Heat disengaged in the formation of binoxalate of pot. 8°·28
... ... in saturating acid of binoxalate of pot. 12°·40
20°·68

One-fourth of an equivalent of binoxalate of potash, 22·91 grains, containing 6·25 grains of water of crystallization, was dissolved in 1538 grains of water at 64° F., with a fall of 1°·65, 1°·66, 1°·65; mean 1°·65 F. The mean result multiplied by four, gives 6°·60 F. as the fall on dissolving a whole equivalent of binoxalate of potash in water. This is 0°·89 more than the sum of the falls on dissolving the constituent salts separately, 2°·66 + 3°·05 being equal to 5°·71 only.

Quadroxalate of Potash. $KO, C_2O_3 + HO, C_2O_3 + 2(HO, C_2O_3 + 2HO)$.—Four-sixths of an equivalent of hydrated oxalic acid, 26·22 grains, were mixed with one-sixth of an equivalent of potash exactly to form this salt:—

Before mixture . .	64°·25	64°·23	64°·25
After mixture . . .	66°·01	66°·01	65°·99
Rise of temperature .	1°·76	1°·78	1°·74

The mean result 1°·76 multiplied by six, gives 10°·56 as the heat evolved in the formation of quadroxalate of potash; that is, in the saturation of 1 equivalent of potash by 1 of oxalic acid, and the further combination of that oxalate of potash with 3 equivalents of oxalate of water. This rise of temperature is nearly the same as that in the formation of neutral oxalate of potash, namely 10°·48.

To observe the heat disengaged on neutralizing quadroxalate of potash by hydrate of potash, one-sixth of an equivalent of that acid salt in solution was mixed with three-sixths of an equivalent, or rather more, of the alkali, so as to form neutral oxalate:—

Before mixture . .	64°·19	64°·20	64°·51
After mixture . . .	69°·38	69°·42	69°·71
Rise of temperature .	5°·19	5°·22	5°·20

Doubling 5°·20, the mean result, we have 10°·40 F. as the heat disengaged on saturating 1 equivalent of potash by each of the 3 atoms of oxalate of water in the quadroxalate of potash.

0·192 equivalent (30·70 grains) of quadroxalate of potash was dissolved in 1540 grains of water at 63°, with a fall of 2°·02, 2°·13, 2°·14; of which the mean is 2°·10 F. This gives by calculation a fall of 10°·93 for the solution of a whole equivalent of quadroxalate of potash, which is 0°·88 less than the fall of its constituent salts dissolved separately, 2°·66 with three times 3°·05 amounting to 11°·81.

The different oxalates enumerated appear to absorb quantities of heat, on dissolving, which have a simple relation to each other. Thus, dividing the different falls of temperature by 0°·88, a number which has more than once presented itself in the discussion of these experiments, we obtain a set of ratios given in the second column; and which, being multiplied by two in the third column, approach nearly to round numbers:—

	I. Cold on solution.	II. Ratios.	III. Ratios.	
Cr. oxalate of potash . .	2°·66	3·02	6·04	6·
Cr. oxalic acid	3°·05	3·47	6·94	7·
Cr. binoxalate of potash .	6°·60	7·50	15·00	15·
Cr. quadroxalate of potash	10°·93	12·42	24·84	25·

VI. *Neutralization of Bicarbonate of Potash with Hydrate of Potash.*

Half an equivalent of the crystallized salt, 31·38 grains, dissolved in water, was neutralized with hydrate of potash:—

Before mixture . .	67°·28	67°·93	67°·68
After mixture . . .	70°·66	71°·24	71°·03
Rise of temperature .	3°·38	3°·31	3°·35

Doubling 3°·35, the mean result, there is obtained 6°·70 as the heat disengaged on saturating the second proportion of carbonic acid in the bicarbonate of potash.

One equivalent, 62·76 grains, of the crystallized bicarbonate was dissolved in 100 grammes of water at 67°, with a fall in three experiments of 3°·68, 3°·69 and 3°·74; mean 3°·70.

One equivalent of anhydrous carbonate of potash was dissolved in 100 grammes of water at 67°, with a rise in three experiments of 2°·48, 2°·43 and 2°·47; mean 2°·46. The heat evolved on dissolving anhydrous acetate of potash is nearly the same, being 2°·45.

VII. *Neutralization of Arsenic and Phosphoric Acids by Hydrate of Potash.*

Half an equivalent of arsenic acid, 36·00 grains, in solution as usual, was mixed with exactly half an equivalent of hydrate of potash, to form the binarseniate of potash ($2HO, KO, AsO_5$):—

Before mixture . .	63°·04	63°·19	63°·29
After mixture . . .	68°·14	68°·30	68°·38
Rise of temperature .	5°·10	5°·11	5°·09

Doubling 5°·10, the mean result, we obtain 10°·20 F. as

the heat disengaged by neutralizing 1 equivalent of potash in the formation of binarseniate of potash.

One-fourth of an equivalent of arsenic acid, 18·00 grains, was mixed with exactly half an equivalent of potash, to form arseniate of potash ($HO, 2KO, AsO_5$):—

Before mixture . .	63°·27	63°·33	63°·42	
After mixture . . .	67°·87	67°·94	68°·05	
Rise of temperature .	4°·60	4°·61	4°·63	Mean 4°·61.

Twice 4°·61, or 9°·22 F., is therefore the heat disengaged on neutralizing 1 equivalent of hydrate of potash in the formation of the neutral arseniate of potash.

The same salt was formed by mixing together solutions of half an equivalent of binarseniate of potash, 56·37 grains, and exactly half an equivalent of potash:—

Before mixture . .	64°·28	64°·27	64°·20
After mixture . . .	68°·31	68°·33	68°·26
Rise of temperature .	4°·03	4°·06	4°·06

Taking 4°·05 as the mean, we have twice that quantity, or 8°·10 F., as the heat disengaged on neutralizing 1 equivalent of potash with the acid in binarseniate of potash.

On forming the subarseniate of potash ($3KO, AsO_5$), by mixing together solutions of one-sixth of an equivalent of arsenic acid and exactly half an equivalent of potash:—

Before mixture . .	63°·41	63°·50	63°·50
After mixture . . .	67°·40	67°·52	67°·49
Rise of temperature .	4°·09	4°·02	3°·99

Doubling 4°·03, the mean result, we have 8°·06 F. as the heat disengaged in the formation of one-third of an equivalent of subarseniate of potash, or in the neutralization of each of 3 equivalents of potash by a single equivalent of arsenic acid.

Hence the successive addition of 3 equivalents of potash to 1 of arsenic occasions the following disengagements of heat:—

By first	KO	10°·20; formation of binarseniate of potash.
... second	KO	8°·10; formation of arseniate of potash.
... third	KO	5°·88; formation of subarseniate of potash.
		24°·18 = 8·06 × 3.

Of hydrated phosphoric acid, which had been boiled in water for a considerable time to render it fully tribasic, half an equivalent was mixed with half an equivalent of potash, to form biphosphate of potash ($2HO, KO, PO_5$):—

Before mixture . .	64°·00	64°·00	64°·03
After mixture . . .	69°·01	68°·99	69°·02
Rise of temperature .	5°·01	4°·99	4°·99

Taking 5°·00 as the mean, we have 10°·00 F. as the heat disengaged on saturating 1 equivalent of potash with 1 equivalent of phosphoric acid in the formation of biphosphate of potash, containing KO + 2HO as bases.

By mixing one-fourth of an equivalent of phosphoric acid with half an equivalent of potash, phosphate of potash (HO, 2KO, PO_5) was formed:—

Before mixture . .	64°·00	63°·61	63°·63
After mixture . . .	68°·49	68°·08	68°·18
Rise of temperature .	4°·49	4°·47	4°·55

Doubling the mean result, 4°·50, we have 9°·00 F. as the heat disengaged in forming half an equivalent of neutral phosphate of potash, or in saturating each of 2 equivalents of potash by 1 equivalent of phosphoric acid, in the formation of phosphate of potash.

The same phosphate of potash was formed by mixing solutions of half an equivalent of biphosphate of potash with half an equivalent of potash:—

Before mixture . .	64°·06	64°·14	64°·15
After mixture . . .	68°·09	68°·15	68°·16
Rise of temperature .	4°·03	4°·01	4°·01

Doubling 4°·02, the mean result, we have 8°·04 F. as the heat disengaged on saturating an equivalent of potash with the acid of biphosphate of potash.

To form the subphosphate of potash (3KO, PO_5), one-sixth of an equivalent of phosphoric acid, 7·43 grains, was mixed with half an equivalent of potash:—

Before mixture . .	63°·61	63°·67	63°·69
After mixture . . .	67°·87	67°·93	67°·99
Rise of temperature .	4°·26	4°·26	4°·30

Twice the mean result, 4°·27, is 8°·54 F., which is the heat disengaged on neutralizing each of 3 equivalents of potash by a single equivalent of phosphoric acid.

The heat therefore disengaged in the gradual saturation of phosphoric acid by 3 equivalents of potash may be thus distributed:—

By first equivalent of potash . .	10°·00
... second	8°·08
... third	7°·54
	25°·62 = 8·54 × 3.

XCVI. *Note on a Means of Preserving the Crystals of Salts as permanent objects for Microscopic Investigation. By* Robert Warington, *Esq.*

HAVING occasion lately to require the crystals of various salts in a state fitted for examination by polarized light under the microscope, and as the preparation of these crystals was frequently attended with much trouble and loss of time, it became a point of importance to render the object, when once perfected, permanent, so that the investigation of certain individual crystals could be repeated, and additional observations made at any period. This was rendered the more desirable from the difficulty of obtaining perfect and isolated subjects, and the rapidity with which many of these undergo alteration by exposure to the air. With some few salts this operation was comparatively easy, as the Canada balsam offered an excellent medium for the purpose, but in the greater number of cases I have examined it proved totally indifferent; and this arises from two causes, the first from the action of the turpentine contained in the balsam rendering the surfaces of the crystals opalescent; the second, from the heat, which it was necessary to apply to make the balsam sufficiently fluid to displace the atmospheric air, fusing the salt in its water of crystallization, or rendering it opake from the loss of water. Olive oil on trial appeared a good medium for all cases, but was objectionable from its fluidity, and from its depositing its stearine in cold weather. Castor oil was then tried, and this I have adopted with great satisfaction.

The method to be adopted in mounting these specimens is as follows:—A warm saturated solution of the salt required is to be prepared, and a drop of it placed upon the glass slider, on which it is intended to be permanently mounted, and allowed to crystallize; when a good group of crystals is obtained the uncrystallized portion is to be cautiously removed; this is best effected by drawing it gradually away in a small stream along the edge of the slider, having previously broken through that part of the crystalline ring adjacent to the edge; the salt is to be allowed to drain itself quite dry by placing the slider on its end in a vertical position. It should next be examined under the microscope, to ascertain the fitness of the crystals for the purposes required, because many salts separate from their solutions in crystals too thin to exhibit any prismatic colours when viewed by polarized light, appearing only of a pearly or silvery aspect, while others form in the opposite extreme, and are totally unfit, from their thickness, for investigation. Presuming, however, that the crystals are such

as the investigator requires, the next step is to drop on a small quantity of castor oil; that which has been filtered cold must be employed, as otherwise it is liable to the same objection as olive oil, and care must be taken that it covers the whole of the salt, and has displaced all the particles of atmospheric air that may have been adhering to the crystals. This having been done, a small piece of very thin glass is to be carefully placed on the surface of the oil, and any excess which may by this means have been pressed out, cautiously removed by bibulous paper from the edges. Two or three coats of a strong varnish of shell-lac, as ordinary sealing-wax in spirits of wine, or japanners' gold size, are then to be placed round the margin, so as completely to inclose the oil, and the crystals are permanently preserved for observation. It may be perhaps as well to observe, that the one layer of varnish must be allowed to dry for about twenty-four hours before the next is applied, and that during this time the slider must be maintained in a flat position.

February 5, 1844.—E. F. Teschemacher, Esq., in the Chair.

The following presents to the Society's library were announced as having been received since the last Meeting:—

"Abstract of a Memoir on the Chemical Constitution of the Plants of Flax and Hemp," by Robert Kane, M.D., from the author.

"On the Berbeeru Tree;" "On the Medicinal Qualities of the Berbeeru Bark;" "On the Action of the Hydrated Sesquioxide of Iron on Arsenic;" and "On the Constitution of certain Intestinal Concretions," by Douglas Maclagan, M.D., from the author.

The following paper was then read:—

XCVII. *Observations on the Green Teas of Commerce.* *By* Robert Warington, *Esq.*

In examining lately some samples of tea which had been seized, from their being supposed to be spurious, my attention was arrested by the varied tints which the sample of green tea exhibited, extending from a dull olive to a bright greenish blue colour. On submitting this to the scrutinizing test of examination by the microscope with a magnifying power of one hundred times linear, the object being illuminated by reflected light, the cause of this variation of colour was immediately rendered apparent, for it was found that the curled leaves were entirely covered with a white powder having in places a slightly glistening aspect, and these were interspersed with small granules of a bright blue colour, and others of an orange tint; in the folded and consequently more protected parts of the curled leaves these were more distinctly visible. By shaking the whole of the sample mechanically for a short time a quantity of powder was detached, and from this a number of the blue particles were picked out under a magnifying glass, by means of the moistened point of a fine camel's hair pencil. On being crushed in water between two plates of glass they presented, when viewed by transmitted light, a bright blue streak. This change in the method of illuminating the object was necessary for the purpose of seeing the action of the following tests:—A minute drop of a solution of caustic potash was introduced by capillary attraction between the glass plates, and the blue tint was immediately converted to a dark bright brown, and the original blue colour again restored by the introduction of a little dilute sulphuric acid. It was therefore evident that these particles consisted of the ferrocyanide of iron or Prussian blue. The orange granules on examination proved to be some vegetable colouring substance.

To ascertain if possible the nature of the white powder observed on this sample, I separated some of the dust, and heated it to redness with free exposure to the air; the whole of the vegetable matter and Prussian blue was thus destroyed, and a white powder, with a slight shade of brown, was ob-

tained. This dissolved by boiling in dilute hydrochloric acid, and when tested with solution of chloride of barium gave indications of sulphuric acid; it was then evaporated to dryness and again acted upon by very dilute hydrochloric acid; a trace of silica remained undissolved. Solution of ammonia being added threw down a little alumina and oxide of iron, and the ammoniacal solution treated with oxalic acid gave a precipitate of oxalate of lime. A second portion of the powder after calcination was boiled for some time in distilled water, and yielded a solution containing sulphate of lime: this latter substance, therefore, and some other body containing silica, alumina, and perhaps lime, formed the white powder observed. This substance I believe to be kaolin, or powdered agalmatolite, the figure stone of the Chinese. I venture this conjecture not only from the ingredients found, but also from the gloss which the rubbed parts of the curled leaves always assume, and which these materials would be well fitted to produce.

Four or five other samples of green teas were then submitted to the same method of examination, and only one of them proved to be free from these blue granules; this sample was a high-priced tea, and had been purchased about two years; it appeared covered with a very pale blue powder, instead of the white with the blue particles interspersed, as exhibited by the others.

Being still in doubt as to whether this powder and colouring was an adulteration practised in this country or not, I applied to a most extensive wholesale dealer of the highest respectability, and from him obtained a series of samples, each being an average from a number of original chests, and from these I gathered the following results by examination, as before, with the microscope. No. 1. Imperial. The leaf, where seen beneath the superficial coating, was of a bright olive brown colour, with small filaments on its surface; it was covered with a fine white powder and with here and there a minute bright blue particle, at times having the appearance of a stain. No. 2. Gunpowder. Similar to No. 1, but the filaments not visible: this may have arisen from the tight and close manner in which the leaf was curled. No. 3. Hyson. The same as No. 1, the blue particles being perhaps more frequent. No. 4. Young Hyson. The same. No. 5. Twankey. The leaf of this had more of a yellow hue, and was profusely covered with white powder, having the blue particles also more thickly strewn over the surface. It was evident from the examination of these teas that they arrive in this country in an adulterated or factitious state.

On detailing what I had thus found to the friend who had favoured me with the preceding samples, he inquired if I had

examined any *unglazed teas*. This appellation immediately arrested my attention, and I requested to inspect some of them, and found that they possessed externally a totally different aspect, indeed, as far as their colour was concerned, not to be like green teas. They were of a yellow-brown tint without a shade of green or blue, but rather tending on the rubbed parts to a blackish hue. I afterwards received two samples of unglazed teas, specified as of very fine quality, accompanied by two others of the ordinary or, as they are called, in contradistinction, *glazed* varieties, also of a very superior quality. These were therefore immediately submitted to examination. No. 6. Unglazed Gunpowder. It presented the same colour under the microscope as when viewed by the unassisted eye, was filamentous and covered with a white powder inclining to a brown tint, but no shade of blue was visbile. No. 7. Unglazed Hyson. The same as No. 6. No. 8. Gunpowder glazed. Filamentous, covered with a powder of a very pale blue, and the blue granules being but rarely seen. No. 9. Hyson. The same as No. 8. No. 10. Pidding's Howqua, purchased at Littlejohn's at 8*s*. 6*d*. per catty package. This was evidently of the glazed variety; it was filamentous and covered with a pale blue powder interspersed with bright blue granules. No. 11, entitled Canton Gunpowder. This was a splendid sample of the *glazed* variety, as far as colour was concerned; it was more thickly powdered and blued than any that I have examined, and the dust rose from it in quantity when poured from one paper to another. A great many other samples of ordinary green teas were examined, with much the same results; the cheaper teas, or those in general use, and which form the bulk of the imports, being similar to Nos. 5 and 11, and being represented by Twankeys and low-priced Hysons or Gunpowders.

After several unsuccessful experiments, I found that with a little care the whole of this powder or facing, if I may be allowed the term, it being entirely superficial, could be easily removed from the tea, by simply agitating the sample briskly for a few seconds in a phial with distilled water, and then throwing the whole on a lawn or muslin filter, in order to strain the liquid, with the suspended matter, from the leaves as rapidly as possible. After this operation the tea presented a totally altered aspect, as may be supposed; in fact, changing its colour from a bluish green to a bright and lively yellow or brownish yellow tint, and I found that with care it could be redried at a temperature below 212° without even uncurling the leaf, and without apparent loss of any of its characteristic qualities. When the drying was complete the sample appeared nearly as dark as the ordinary black teas, and when

examined by the microscope presented a smooth surface, perfectly free from the previously observed facing, and having all the characters of black tea, with the exception of the corrugated aspect which is common to the greater part of the teas of the latter variety, and which evidently arises from their having been exposed in the operation of drying to a much higher temperature. The greenish-coloured turbid liquid which passed through the meshes of the muslin filter was allowed to deposit the matter suspended in it, which was then washed and collected. These sediments, obtained from various samples, were submitted to the following course of chemical examination. They were, in the first instance, tested with a solution of chlorine gas in water, to ascertain if the colouring material was indigo or other vegetable colour; this substance, as we shall presently see, having been supposed by some persons to be the one employed by the Chinese for the purpose of imparting the blue tint to some of their green teas. In no case, however, that I have yet examined have I found this to be the case; but the colouring agent has invariably proved to be the ferrocyanide of iron or Prussian blue. The presence of this compound was next evidenced by adding a small drop of caustic potash to a little of the sediment under examination, when the green hue was instantly converted to a bright reddish brown, the original blue appearance being again restored by the subsequent addition of a little diluted sulphuric acid. The other ingredients of the facing were sought for in the manner stated in the previous part of this paper, and also by heating a part of the sediment, after calcination and free exposure to the air, with carbonate of soda, to fusion, which, in the case of sulphate of lime being present, formed sulphate of soda and carbonate of lime, and these were each subsequently tested for.

By these means Nos. 5, 8, 10 and 11 were found to be faced with Prussian blue and sulphate of lime. Nos. 6 and 7 gave no indication of Prussian blue, but of sulphate of lime only. The sulphate of lime from some samples appeared to be crystallized gypsum reduced to a fine powder, the coarser particles still exhibiting a crystalline structure.

Through the kindness of Mr. Greene, of the East India House, I was enabled to obtain samples of the Assam teas in a genuine condition; No. 12. Imperial, No. 13. Gunpowder, and No. 14. Hyson. They had none of the blue granules, were very filamentous, and presented the same appearance as the unglazed varieties, but brighter in colour; the facing was apparently sulphate of lime. No. 15. Assam Hyson, of the last importation; it was of the unglazed variety, with the superficial white powder having a slight brown tint, and consisting

of a minute quantity of sulphate of lime with a little alumina.

It appears, therefore, from these examinations that all the green teas that are imported into this country are faced or covered superficially with a powder consisting of either Prussian blue and sulphate of lime or gypsum, as in the majority of samples examined, with occasionally a yellow or orange-coloured vegetable substance; or of sulphate of lime previously stained with Prussian blue, as in Nos. 8 and 9, and one of those first investigated; or of Prussian blue, the orange-coloured substance with sulphate of lime and a material supposed to be kaolin, as in the original sample; or of sulphate of lime alone, as in the unglazed varieties. It is a curious question what the object for the employment of this facing can be; whether, as when sulphate of lime alone is used, it is simply added as an absorbent of the last portions of moisture which can not be entirely dissipated in the process of drying, or whether it is only, as I believe, to give that peculiar bloom and colour so characteristic of the varieties of green tea, and which is so generally looked for by the consumer, that the want of the green colour, as in the unglazed variety, I am informed affects the selling price most materially. This surely can only arise from the want of the above facts being generally known, as it would be ridiculous to imagine that a painted and adulterated article, for such it must really be considered, should maintain a preference over a more genuine one. In looking over the various authors who have written on the subject of tea, I have observed the following curious statements bearing on the above subject, and fully confirming many of my results, and with which I shall close the present communication.

In Dr. Horsfield's valuable translation* on the subject of the manufacture of tea in Java, we find, at page 36, the following dialogue:—

"Visitor. Is it indeed the case that tea is so much adulterated in *China*?

"Superintendent. Unquestionably! but not in the interior provinces, for there exist rigid laws against the adulteration of tea; and all teas, as they come out of the plantations, are examined on the part of government, to determine whether they are genuine; but in Canton, which is the emporium of teas, and especially at Honân, many sorts, indeed most teas, are greatly adulterated, and that with ingredients injurious to health, especially if too much of these ingredients be added. This is especially the case with the *green* tea, in order to improve the colour; and in this manner to add to the value of tea in the eyes of the common consumers.

* Essay on the Cultivation and Manufacture of Tea in Java, translated from the Dutch by Thomas Horsfield, M.D., F.R.S.

"Visitor. Are these ingredients known?

"Superintendent. Most of them are certainly known; they have been communicated to government (we presume the Dutch government), while at the same time the privilege has been requested that they might not be employed here; and although this occasions loss, the request has been granted, and it has been ordered by government that not the least admixture should take place, either to improve the colour or taste of the tea, even in such cases where this might be desirable."

Dr. Royle states*, "The Chinese in the neighbourhood of Canton are able to prepare a tea which can be coloured and made up to imitate various qualities of green tea; and large quantities are thus yearly made up." And Dr. Dickson†,—"The Chinese annually dry many millions of pounds of the leaves of different plants to mingle with the genuine, as those of the ash, plum, &c., so that all spurious leaves found in parcels of bad tea must not be supposed to be introduced into them by dealers in this country. While the tea trade was entirely in the hands of the East India Company few of these adulterated teas were shipped for this country, as experienced and competent inspectors were kept at Canton, to prevent the exportation of such in the Company's ships; but since the trade has been opened all kinds find a ready outlet, and as the demand often exceeds the supply, a manufactured article is furnished to the rival crews."

During these investigations I have received samples of teas, both green and black, imported into this country from China, which are known, by the most experienced brokers, not to contain a single leaf of tea, and which were sold at public sale in bond at from $1\frac{3}{4}d.$ to $2d.$ per pound.

Again,—"The green tea for exportation undergoes some process which changes its colour, giving it a bluish green hue."

Mr. Davis‡ gives the following important information on this subject:—"The tea farmers§, who are small proprietors or cultivators, give the tea a rough preparation, and then take it to the contractors, whose business it is to adapt its further preparation to the existing nature of the demand."

"Young hyson‖, until spoiled by the large demand of the Americans, was a delicate, genuine leaf." "As it could not be fairly produced in any large quantities, the call for it on the part of the Americans was answered by cutting up and sifting *other* green teas through sieves of a certain size; and as the Company's inspectors detected the imposture, it formed no portion of their London importations. But the abuse became still worse of late, for the coarsest *black* tea leaves have been

* Article Thea in the 'Penny Cyclopædia.'

† Article Thea, Medical and Dietetical, 'Penny Cyclopædia.'

‡ Davis's 'Chinese.' § Vol. ii. p. 458. ‖ p. 464.

cut up, and then *coloured* with a preparation resembling the hue of green teas." At page 466 Mr. Davis continues, after speaking of the frauds with spurious and adulterated teas which the Chinese had endeavoured to practise, "But this was nothing in comparison with the effrontery which the Chinese displayed in carrying on an extensive manufactory of *green teas* from *damaged black leaves*, at a village or suburb called Honân."

"The remission of the tea duties in the United States occasioned, in the years 1832 and 1833, a demand for green teas at Canton which could not be supplied by the arrivals from the provinces. The Americans, however, were obliged to sail with cargoes of green teas within the favourable season; they were determined to have these teas, and the Chinese were determined they should be supplied. Certain rumours being afloat concerning the manufacture of green tea from old black leaves, the writer of this became curious to ascertain the truth, and with some difficulty persuaded a Hong merchant to conduct him, accompanied by one of the inspectors, to the place where the operation was carried on." "Entering one of these laboratories of fictitious hyson, the party were witnesses to a strange scene." The damaged black tea leaves, after being dried, were transferred to a cast iron pan placed over a furnace, and stirred rapidly with the hand, "a small quantity of turmeric in powder having been previously introduced; this gave the leaves a yellowish or orange tinge, but they were still to be made green. For this purpose some lumps of a fine blue were produced, together with a substance in powder, which, from the names given to them by the workmen, as well as their appearance, were known at once to be *Prussian blue* and *gypsum*. These were triturated finely together with a small pestle, in such proportions as reduced the dark colour of the blue to a light shade; and a quantity equal to a teaspoonful of the powder being added to the yellowish leaves, these were stirred as before over the fire, until the tea had taken the fine bloom colour of hyson, with very much the *same scent*. To prevent all possibility of error regarding the substances employed samples of them were carried away from the place. The Chinese seemed quite conscious of the real character of the occupation in which they were engaged; for, on attempting to enter several other places where the same process was going on, the doors were speedily closed upon the party. Indeed, had it not been for the influence of the Hongist who conducted them, there would have been little chance of their seeing as much as they did*." "It is an interesting and important question to determine whether the

* Vol. ii. p. 468.

same system of artificial colouring enters at all into the manufacture of the more genuine green teas brought to this country." "One fact is well ascertained and undeniable, that the Chinese themselves do not consume those kinds of green teas which are prepared for exportation*." "The young hyson and Pekoe teas, made from the green tea plant, have a yellower and as it were a more *natural* hue than the bluish-green that distinguishes the elaborated teas imported to us."

Mr. Bruce states † that in the last operation for colouring the green teas "a mixture of sulphate of lime and indigo, very finely pulverized and sifted through fine muslin, in the proportion of three of the former to one of the latter, is added to a pan of tea containing about seven pounds, about half a tea spoonful of this mixture is put, and rubbed and rolled along with the tea in the pan for about an hour. The above mixture is merely to give it a uniform colour and appearance. The indigo gives it the colour, and the sulphate of lime fixes it. The Chinese call the former *Youngtin*, the latter *Acco*."

Indigo however, as previously stated, has never yet been met with on any of the green teas of commerce that have fallen under my notice.

The following curious observation occurs in Maculloch's 'Commercial Dictionary:'—"Blue is a favourite colour with the Chinese; and in 1810—11 the imports of Prussian blue into Canton from England amounted to 253,200 pounds. But for some years past the Chinese have not imported a single pound weight. The cause of the cessation of the trade deserves to be mentioned. A common Chinese sailor, who came to England in an East Indiaman, having frequented a manufactory where the drug was prepared, learned the art of making it, and on his return to China he established a similar work there with such success that the whole empire is now supplied with native Prussian blue."

February 19, 1844.—The President in the Chair.

The Council declared the names of the gentlemen whom they proposed should retire from the Vice-Presidents and Council, and those whom they proposed for election, in accordance with Law 8.

The following communications were then read:—

XCVIII. *Account of a new Cyanide of Gold.*

By Mr. John Carty.

THERE is one compound of cyanogen and gold known at present to chemists; it is a tercyanide, or contains 3 equi-

* Vol. ii. p. 469.

† Report on the Manufacture of Tea, and on the extent and produce of the Tea Plantations in Assam, by Mr. C. A. Bruce, Superintendent of Tea Culture, presented to the Tea Committee, August 16, 1839.

valents of cyanogen combined with one of gold. Having observed indications of a protocyanide, and not finding it mentioned in the chemical works usually referred to, I tried to obtain it pure, and have, I believe, succeeded by the following method:—

Protochloride of gold was decomposed by cyanide of potassium in solution. An abundance of a yellow matter appeared at first, but an excess of the cyanide gave a clear and perfect solution. To this solution muriatic acid in excess was added; on boiling a bright yellow powder precipitated, which was washed and dried by a moderate heat. It was insoluble in water, alcohol and æther; soluble in ammonia and in solution of cyanide of potassium. It was decomposed by heat, like a cyanide, and nothing but cyanogen gas was driven off. It was not decomposed by strong boiling muriatic or nitric acid, or by a solution of chlorine, but was decomposed, though not rapidly, by hot nitro-muriatic acid, and very slowly by solution of potash; boiling sulphuric acid liberated metallic gold.

30·7 grains of the yellow powder were heated to redness in the air, 27·0 of gold remained, 3·7 of cyanogen were therefore driven off. Other experiments on smaller quantities agreed closely with this, and they show the yellow substance to have been composed as near as may be of 200 of gold and 26 of cyanogen; and it is therefore a protocyanide of gold.

When tercyanide of gold was dissolved in boiling muriatic acid, and the solution concentrated, protocyanide of gold was gradually deposited as a yellow powder. 2 atoms of cyanogen were removed, probably by forming ammoniacal compounds with the elements of the water which is present.

The protocyanide of gold was dissolved in hot ammonia; on cooling an abundance of gray glistening plates fell, which were found to be a compound of the protocyanide and ammonia. The ammonia was easily removed by a gentle heat, or by hot muriatic acid leaving the protocyanide.

Protocyanide of gold was dissolved in solution of cyanide of potassium. By evaporating the liquid, long prismatic white crystals, nearly opake, anhydrous and somewhat deliquescent, were obtained. They were decomposed by heat into gold, cyanogen gas and cyanide of potassium. A solution of them was not soon affected by muriatic acid in the cold, but on boiling the liquid for a minute or two protocyanide of gold was precipitated, and no gold remained in solution. By analysis it appeared to consist of one equivalent of protocyanide of gold with 2 of cyanide of potassium *.

* After the reading of this paper before the Chemical Society, a paper on the same cyanide of gold, by Messrs. Glassford and Napier, was read, in which the composition of the double cyanide of potassium and gold was

From these experiments we may conclude,—1. That there is a protocyanide of gold remarkable for being the most stable of all the cyanides, except perhaps cyanide of palladium. 2. That tercyanide of gold is reduced to protocyanide by boiling muriatic acid. 3. That the protocyanide combines with ammonia and with cyanide of potassium.

XCIX. *On the Cyanides of the Metals, and their Combinations with Cyanide of Potassium.* Part I. *Cyanide of Gold.*

By Messrs. Charles F. O. Glassford *and* James Napier.

1. THE various compounds which cyanogen forms with the metals constitute one of the most interesting class of bodies which the science of chemistry can produce; and the rapid progress of electro-metallurgy, with the almost universal use of these cyanides in the practice of this art, adds a double interest to the study of these compounds with the alkaline cyanides. Indeed, we might have expected that long before this some definite information would have been published upon the nature, constitution and easy preparation of these salts, as yet however, so far as we are aware, nothing complete has appeared. With a view to remedy this, and to facilitate a full investigation of the subject, we have drawn up the following observations, the result of extensive practical operations in the art of electro-metallurgy, which we beg to present to the Chemical Society, in the hope that our results, in connexion with those of others who may be labouring in the same field, may lead to a more precise knowledge of their character and constitution.

2. In systematic works on chemistry reference is made to this subject in a very general way. The sum of such information may be thus expressed:—"The soluble cyanides of the alkaline metals, potassium, sodium, &c., dissolve the insoluble cyanides of the metals proper, forming double salts, which are generally crystallizable:" the probable constitution of only a very few of these salts are given.

3. From the researches of L. Gmelin upon the metallo-cyanurets, which were published many years ago, it would appear that there are two classes of compounds in which other metals are found to replace the iron in the yellow and red prussiate of potash, and to form indeed metallo-cyanurets and sesquicyanurets of potassium, &c. There seems however to be a singular indefiniteness on this subject in chemical works; for Turner, in his 'Elements,' 5th edition, p. 779, says, that

stated to be 1 eq. of protocyanide of gold, 1 of cyanide of potassium and 1 of water, and on carefully repeating my analysis I found their statement to be correct.

" L. Gmelin has obtained a double cyanuret of zinc and potassium, in which the zinc acts as iron in the ferro-cyanurets." He also says, " that a cobalto-cyanuret of potassium, and similar double cyanurets of nickel and cobalt, may be prepared in the same manner as the preceding salt;" and further, " that Gmelin procured the cobalto-cyanuret in yellow crystals, similar in composition and form to ferro-cyanuret of potassium." The salts here described are evidently analogous to the yellow prussiate of potassa, or ferro-cyanuret of potassium; but on referring to Professor Graham's 'System,' we find there described salts of cobalt, chromium and manganese, not analogous to yellow prussiate of potash, but similar in symbolic constitution to the red prussiate of potash, that is, metallo-sesquicyanurets having a supposed salt radical in which these metals replace iron to the formation of cobalti-, chromi-, and mangani-cyanogen; no mention is made whatever of the existence of compounds similar to yellow prussiate of potash, or of a cobalto-, chromo-, and mangano-cyanogen.

On turning to Berzelius's *Traité*, tome ii. p. 115, we find a description of the same zinco-cyanuret of potassium, or, as he names it, cyanuri zincoso-potassique, analogous in composition to the yellow prussiate of potassa, in which zinc is found to replace iron. He says, " The existence of this salt, of which the discovery is due to L. Gmelin, leads us to presume that zinc has a series of double cyanurets, like iron, nickel, &c." Here also Berzelius corroborates the statement made by Dr. Turner, and speaks of these compounds as analogous to the yellow prussiate of potassa, or as metallo-cyanurets. Turner mentions (p. 780) that Gmelin's observations upon the nickel, copper and zinco-cyanurets have been confirmed by a late pupil of his, Mr. F. Rodgers, and his brother; on referring to their Memoir, published in the Philosophical Magazine of February 1834, we find a different statement from what Dr. Turner makes; they say, " L. Gmelin prepared a double cyanuret of cobalt and potassium, analogous to the red cyanuret of iron and potassium." These different statements of apparently the same thing must have arisen either from the want of proper care in naming the salts, so as to indicate to which class they belong, or to the want of sufficient evidence respecting their constitution. We may render this still more evident by the following statements. Berzelius mentions a cyanure platinoso-potassique, or platino-cyanuret of potassium, but on referring to its alleged constitution, we do not find, as its name indicates, a compound of platina similar to the ferro-cyanuret of potassium, but a compound totally different from either the yellow or red prussiate of potassa; the same salt is

described in Graham's 'Elements,' p. 991; and there also it is called the platino-cyanide of potassium. The acid described in some chemical works as the platino-cyanic acid, does not resemble in constitution the ferro-cyanic acid, as its name indicates. If, therefore, there be a necessity for distinguishing the acid formed by the supposed salt radical ferri-cyanogen with 3 eqs. of hydrogen, from that formed by ferro-cyanogen with 2 eqs. of hydrogen, so then there is an equal necessity for distinguishing a metallo-cyanogen, which combines with 2 eqs. of hydrogen, from a metallo-cyanogen, which combines with 1 eq. of hydrogen: for the same reason also platino- and other cyanides of potassium should receive appellations which indicate their constitution, and not such as by analogy lead us to infer a totally different constitution. These remarks tend to show us the necessity of carefully re-examining the nomenclature of this apparently complex subject, and the scrupulous care with which we ought to classify and name these compounds, so as neither to misrepresent their constitution, nor to leave the possibility of their being ascribed to classes to which they do not belong.

4. We deem these observations necessary for the purpose of alluding to a memoir by Mons. A. Meillet, which appeared in the *Journal de Pharmacie et de Chemie* for June last, and which was translated into the Philosophical Magazine for August, entitled, "On some new combinations of Cyanogen." The author says, "The peculiar manner in which cyanogen acts towards iron, by forming two very stable acids with it, leads to the supposition that it is not the only metal with which cyanogen is capable of combining. In fact, some German chemists, and Gmelin among others, have discovered three new compounds, which are platino-cyanogen, cobalto-cyanogen, and chromo-cyanogen, and afterwards the hydrogenated acids analogous to ferro-hydrocyanic acid, and several other metallic salts." Here again we have more evidence of the singular confusion with which this subject has become invested. If we are to accept these names for what they express, and as yet we have no reason to do otherwise, we must infer that these metallo-cyanogens are analogous to the ferro-cyanogen; but this is not the case, for we have just shown that platino-cyanide of potassium is not similar in constitution to the ferro-cyanide of potassium. Meillet then proceeds to say, "that the processes employed by these chemists were somewhat complicated, and they had not continued their experiments;" the method which he employed, he says, "is simple, and there may be procured by it a great number of perfectly definite compounds." The remainder of the paper

is taken up with a brief description of the characteristics of these salts; among others he mentions the auro-, the argento- and the cupro-cyanides of potassium, classifying these under their supposed salt radicles, as auro-cyanogen, argento-cyanogen, and cupro-cyanogen. It is in the consideration of these various metallic combinations with cyanogen, that we have made the following investigations. Before commencing the detail of these, we must offer a few observations upon the cyanide of potassium as usually prepared, and as employed by Meillet in his experiments.

5. The cyanide of potassium which is employed by us in our daily operations is prepared according to the process first pointed out by Messrs. F. and E. Rodgers, now generally known by the appellation "Liebig's Process;" from what particular cause it came to be so named we know not, unless it may have been that the publication of this process by Professor Liebig occurred at a time when the attention of practical and scientific men were more particularly drawn towards an attentive consideration of this compound, from its important applications in chemical analyses, and its extensive employment in the new art of electro-metallurgy. To show, however, that this process was known long before this illustrious chemist pointed it out, we may be allowed to quote the following passage from the memoir of Messrs. Rodgers, already mentioned as having been published in the Philosophical Magazine for February 1834. After detailing the various processes then known, and others which they had discovered, they describe this process as follows:—"Cyanuret of potassium may be prepared by exposing a mixture of anhydrous carbonate of potash and anhydrous ferro-cyanuret of potassium to a moderate red heat, in a covered porcelain crucible, for about twenty minutes." "The proportions employed should be nearly 1 eq. of anhydrous carbonate of potash to 1 eq. of the anhydrous ferro-cyanuret of potassium. The process is very productive, for the weight of the cyanuret of potassium obtained by this process is much greater than the weight of the cyanuret obtained by heating ferro-cyanuret of potassium alone, owing to the cyanogen of the cyanuret of iron uniting with the potassium contained in the carbonate of potash; and, moreover, the process occupies less time. Some carburet of iron always remains in the crucible."

6. Cyanide of potassium may be obtained pure for experimental investigation in the laboratory by the use of absolute alcohol; but where hundred weights are prepared and used at a time this is not admissible. As employed in the arts it contains many impurities: these are chiefly cyanate, carbonate,

muriate and sulphate of potash, silica, and yellow prussiate of potash. The average amount of these impurities is 35 per cent., often as high as 50 per cent. It contains much silica when prepared, as is usually directed, in earthenware crucibles; and when the exact proportions of the yellow prussiate of potash or carbonate of potash are not employed; when these are not perfectly anhydrous, salts of ammonia are generated; and when commercial carbonate of potash is used, muriate and sulphate of potash. Even when the materials are employed chemically pure and perfectly anhydrous, it contains 20 per cent. of cyanate of potash; this, according to Professor Liebig, is of little consequence in the ordinary operations of testing, but in respect to analytical inquiry, and to electro-metallurgical operations, we find it of the greatest importance. As however we shall have opportunities of pointing these out in detail, we only allude to them here in a general way.

7. When nitrate of silver is added to solution of cyanide of potassium, just so long as the precipitate which is at first formed is redissolved, we obtain the *whole* of the cyanide of potassium in union with the silver, none of the other salts present, although amounting to a large per-centage, taking any part in the action. Upon this law we have founded a method of estimating the exact quantity of pure cyanide of potassium in any sample; as, however, the principle upon which this depends can be better explained when the nature and constitution of the cyanide salt of silver is described, we shall return to it when treating of that metal.

8. As when one eq. of chloride of gold combines with one eq. of chloride of potassium, a double salt, called chloride of gold and potassium, is formed, so shall we call the union of one eq. of cyanide of gold with one eq. of cyanide of potassium the "cyanide of gold and potassium," and apply similar names to the other metallic salts having a like constitution. The terms double cyanides, bicyanides, &c., which are usually given to such compounds, we consider neither necessary nor sufficiently expressive.

9. The equivalent numbers employed are those given in Dr. Turner's 'System,' namely,—Cyanogen 26·39, potassium 39·15, cyanide of potassium 65·54, gold 199·20, cyanide of gold 225·59.

10. *Cyanide of Gold.*—Little is said in any systematic treatise of the cyanide of gold. Berzelius, almost the only chemist who mentions this compound, says, "That this salt presents itself under the form of a pale yellow substance, insoluble in water, which is obtained by precipitating the chloride of gold with cyanide of potassium, and gives as its composition the

formula Au, Cy_3." Kane also mentions this pale yellow compound, and gives it the same composition. It may readily be obtained by decomposing the chloride of gold with cyanide of potassium, but both solutions must be saturated, and care must be taken not to add an excess of cyanide of potassium; the product however by this process is very small compared to the quantity of gold employed, and it is necessary to proceed as follows to obtain the whole of the gold as cyanide:— Saturated solutions are to be used, and a slight excess of cyanide of potassium added, so as to redissolve the cyanide of gold; the whole is to be evaporated to perfect dryness, treated with nitric or muriatic acids to decompose the cyanide of potassium, again evaporated to dryness, and gently heated so as to expel the excess of acid, when cold water is to be added, and the whole thrown upon a filter and thoroughly washed. Obtained in this way however it generally contains a portion of silica, particularly if the cyanide of potassium has been prepared in earthenware crucibles; and to obtain the cyanide pure we have recourse to other methods. The best process is to decompose the cyanide of gold and potassium. The salt is to be dissolved in a small portion of distilled water, nitric or muriatic acid added, and the liquid brought to a boiling heat, the cyanide of gold then precipitates; but it is necessary to expel the excess of acid by evaporation before the whole of the cyanide is obtained; the dry mass is then treated with water, thrown upon a filter and well washed.

The cyanide of gold obtained by the last method is of a beautiful canary yellow colour, which is not affected by exposure to light, or by the action of acids: it is an exceedingly fine powder, and readily passes through a single filter; it is insoluble in caustic potash and water; is slightly soluble in nitric, muriatic, and sulphuric acids when recently precipitated; is soluble in ammonia, hyposulphite of soda, and readily so in cyanide of potassium; when fused at a red heat with carbonate of potash, it is entirely decomposed, and the gold may be obtained in a bright metallic button.

11. The cyanide obtained by the decomposition of the double salt by acids was examined in this way and the following results obtained:—

10 grs.	yielded	8·82 grs.	of gold	= 88·20	per cent.
15 grs.	...	13·23 grs.	...	= 88·20	...
7 grs.	...	6·17 grs.	...	= 88·14	...

These results approximate so very closely to the calculated result, viz. 88·30 per cent., that we are at once led to the conclusion that it is a true proto-cyanide, the constitution of which is represented by Au + Cy.

A cyanide of the constitution represented by Berzelius and Kane would contain only 71·56 per cent.

The cyanide of gold obtained by the first process is generally contaminated, as already mentioned, with silica and a small portion of iron, obtained from the cyanide of potassium employed: these impurities will vary according to the state of the cyanide used. Before these facts were ascertained the analyses of the cyanide of gold yielded the following very variable results,—85·00 per cent., 85·50 per cent., 85·57 per cent.; this last sample, when thoroughly washed with water, carefully dried and examined, gave still only 86·00 per cent.

12. *Cyanide of Gold and Potassium.*—This salt, which is that now so extensively employed in gilding by the electric force, may be obtained by various processes:—1. By dissolving the cyanide of gold, prepared by the first process just given, in cyanide of potassium. 2. By dissolving oxide of gold in cyanide of potassium. The oxide of gold is prepared for this purpose by digesting calcined magnesia in nitro-muriate of gold, as is well known; as it is very apt to retain a portion of magnesia as usually prepared, it is better to boil the oxide so obtained in strong nitric acid, to filter through close muslin or calico, allowing the green nitrate solution to fall into a large quantity of distilled water. The oxide of gold is thus obtained quite pure, and as a very bulky reddish-brown precipitate, which when dried contracts, and becomes of a pale brownish-yellow colour: it dissolves readily in cyanide of potassium, with the assistance of a little heat, or by digestion, and constitutes the salt in question. 3. It may also be obtained, as already mentioned, by adding a solution of cyanide of potassium to terchloride of gold until the solution becomes colourless. As the reactions which take place with these solutions are exceedingly interesting, and calculated to add evidence to the existence of a hitherto unobserved law, which will be fully brought out when treating of the double silver salt, and to explain similar reactions with platina and other metals, we will endeavour to follow them.

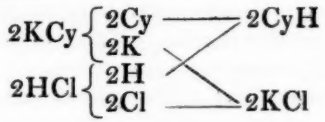
13. When a saturated solution of cyanide of potassium is added, in small portions, to a cold and strong solution of nitromuriate of gold, there is at first a violent effervescence, the solution becomes slightly turbid, and then quite transparent. The reaction may be explained as follows:—

The first effect is the neutralization of the excess of nitric and muriatic acids contained in the nitro-muriate of gold. This results at the expense of the cyanate of potash and cyanide of potassium.

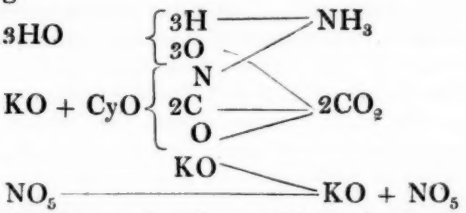
Thus—$2KCy + KO, CyO + 2HCl + NO_5 + 3HO$,
producing

$$2KCl + KONO_5 + 2CO_2 + NH_3 + 2CyH,$$

or represented thus:



and forming—



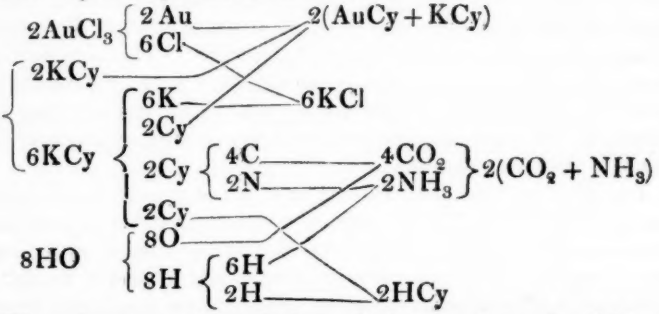
The solution is now free from acid; and on a further addition of cyanide of potassium it immediately, by the assistance of water, reacts upon the terchloride of gold. This will be evident from the following formulæ,

$$2AuCl_3 + 8KCy + 8HO,$$

producing

$$2(AuCy + KCy) + 6KCl + 2(NH_3 + CO_2) + 2HCy,$$

or it may be represented thus:—



When, however, the solution of nitro-muriate of gold is recently prepared, saturated and hot, a portion of the ammonia formed reacts upon a portion of the gold, forming aurate of ammonia, which precipitates along with the cyanide of gold; on the addition of cyanide of potassium the ammonia is liberated and the double salt of gold and potassium is produced.

14. The following process which we have employed is beautifully calculated for obtaining a large quantity of salt in a very few hours, and at comparatively little trouble.

A solution of cyanide of potassium is prepared, which contains about six times as much cyanide as the quantity of gold wished to be dissolved. The cyanide may be dissolved in twice, thrice or four times its weight of distilled water and carefully filtered to separate any insoluble matters with which the cyanide is usually contaminated; this solution is then to be gently and carefully raised to a temperature of 100° F. in an earthenware or glass vessel. Two plates of gold are placed in the solution at the opposite sides of the vessel, and these connected by means of copper wires to the poles of a small galvanic battery, composed of two or three pairs of zinc and copper plates, and excited with dilute acid. As soon as the circuit is completed the operation commences, gold is dissolved from that plate connected with the copper end of the battery, passes into the solution, and is only partly deposited upon the opposite plate, whilst a gentle flow of gas is evolved from the negative pole. The solution of cyanide of potassium rapidly consumes the gold which is dissolved at the positive pole and becomes a double salt of cyanide of gold and potassium. The gold which deposits upon the negative pole is in minute grains, occasionally quite brown, and is beautifully crystalline. The operation is much facilitated by having the positive pole or plate of gold several times larger than the opposite plate. At first the amount of gold deposited is very small compared with that dissolved from the positive pole, the solution retaining the greater proportion; but after some hours, as the solution becomes saturated, the amount deposited increases until there is a perfect balance. The solution is now to be filtered and carefully evaporated; it yields an abundant crop of crystals of the double salt. In this way half an ounce of gold may be dissolved in a few hours, and nearly an ounce of the salt obtained.

15. The salt obtained by either of these processes presents the same general appearance and constitution. It crystallizes in very minute octahedrons, which cluster together so as to form long, jagged, irregular prisms, which again group round a centre and form starlike masses; they possess a peculiar bitter and metallic taste. They are perfectly colourless and transparent, but seem opake from being composed of numerous small crystals. They are soluble in four times their weight of cold water, and in less than their own weight of boiling water, in the proportion of 5 to 4. They are very sparingly dissolved by alcohol, and their solubility is not increased by boiling. When alcohol is added to a warm saturated solution of the crystals, the salt falls in fine white brilliant shining scales, which are quite opake. Their solution does not stain

the hands by the action of light, neither is the solution affected by exposure to light. When nitric, muriatic, or sulphuric acid is poured over the crystals, they are not affected at first, but by standing some time they are quite decomposed, and cyanide of gold results. The cyanide of gold occasionally precipitates in minute shining crystals from the nitric solution. Their solution is not immediately effected in the cold by these acids, but a boiling temperature decomposes them, the yellow cyanide of gold precipitating. Tartaric, oxalic and acetic acids effect the same decomposition when boiled. The nitric, muriatic and sulphuric acids added to a cold saturated solution precipitate the salt undecomposed. The following metallic solutions were added to a solution of the salt, and the results were as follows:—

Nitrate of copper . . a white precipitate of the mixed cyanides.
Sulphate of zinc . . . .
Nitrate of silver . . . .
Nitrate of mercury . a yellow-white precipitate ...
Acetate of lead . . . a white precipitate ...
Protosulph. of iron . a white precipitate of the mixed cyanides, which changes to a purplish-blue on the addition of nitric acid.
Muriate of manganese . . . . . small crystals appear on the sides of the glass on standing.
Muriate of tin . . . . a slight opacity, increasing to a precipitate on standing.

When exposed to a red heat with their own weight of carbonate of potash, the whole of the gold is obtained in the metallic state as a bright button. The carefully dried salt was treated in this way and the following results obtained:—

16. A salt prepared with oxide of gold and cyanide of potassium yielded the following results:—

7 grs.	yielded	4·67 gold	= 66·71	per cent.
5 grs.	...	3·33 ...	= 66·66	...
10 grs.	...	6·63 ...	= 66·30	...

The salt prepared by the battery process was also examined: it gave the following results:—

20 grs.	yielded	13·32 gold	= 66·60	per cent.
20 grs.	...	13·25 ...	= 66·25	...

A sample of the former salt was carefully recrystallized, and placed for some time under a receiver over oil of vitriol; it gave the following result:—

20 grs. yielded 13·35 of gold = 66·75 per cent.
The mean of these results is . . . . . 66·54 ...

10 grs. of the salt were treated with nitric acid, and, the acid being completely expelled by evaporation, they were carefully collected and dried, yielded 8·85 grs. of cyanide of gold = 88·50 per cent.

The calculated amount of gold and of cyanide of gold contained in a salt consisting of single equivalents of cyanide of gold, cyanide of potassium and water, is of gold 66·37, and of cyanide of gold 88·30.

Our results approximate so closely to the calculated result, that we consider ourselves warranted in giving the formula

$$AuCy + KCy + HO.$$

17. In conclusion we may add, that from these results we have no hesitation in saying, that the salt described by Meillet as prepared by saturating chloride of gold with cyanide of potassium is not the auro-cyanide of potassium, but the cyanide of gold and potassium as described above.

March 4, 1844.—Robert Porrett, Esq., Treasurer, in the Chair.

Mr. Ferguson presented to the Society's Museum a portion of a candle which was taken from the green sand of the London clay, where it had been for upwards of twenty years.

The following paper was then read:—

XCIX. *On the Cyanides of the Metals, and their Combinations with Cyanide of Potassium.* Part II. *Cyanide of Silver.* *By Messrs.* Charles F. O. Glassford *and* James Napier.

THE compound that is formed by the union of cyanogen with silver has been long known, and its composition ascertained to be 1 equivalent of silver with 1 equivalent of cyanogen. The method of preparing this salt, as given in most chemical works, is by adding hydrocyanic acid to the nitrate or any other soluble salt of silver, when the cyanide of silver falls as a white precipitate. This method we have found, on the large scale, to be both disagreeable and tedious, and have therefore adopted the following method for its preparation. To a neutral solution of nitrate of silver is added cyanide of potassium so long as a precipitate is formed. No hydrocyanic acid is given off, the precipitate being washed from the nitrate of potash may be used for any purpose required. If the cyanide of potassium, however, contains any cyanate or carbonate, they form impurities in the precipitated cyanide of silver; these can be separated by digesting the precipitate for a short time in dilute nitric acid: but if the cyanide of potassium contains any chlorides or undecomposed ferrocyanide, these impurities cannot be separated by this

means. The best method of obtaining cyanide of silver free from all these impurities, is to add a solution of nitrate of silver to a solution of the crystals of cyanide of potassium and silver. Pure cyanide of silver precipitates, although the cyanide of potassium originally used contained all the impurities before enumerated.

The cyanide of silver should not be dried at a heat exceeding 260°, as it assumes a brownish colour when exposed to a higher temperature. It also becomes brown by exposure to light.

Hydrochloric acid converts the cyanide of silver into the chloride with the rapid evolution of hydrocyanic acid.

Nitric acid has no effect upon it except when concentrated and boiling.

Sulphuric acid diluted with its own volume of water decomposes the cyanide of silver when boiling, with the escape of hydrocyanic acid, and the formation of sulphate of silver, which crystallizes by cooling, or slight dilution with water; by this means the cyanide may be separated from the chloride, which is not soluble in sulphuric acid.

Cyanide of silver is soluble in the alkaline chlorides, and in the chlorides of calcium barium and magnesium when boiled, though it is but slightly soluble in these latter when cold. It is also soluble in ferrocyanide of potassium, forming one or two distinct salts easily crystallized, but which we have not yet sufficiently investigated to warrant a more particular notice of them at present. It dissolves freely in hyposulphite of soda, forming a crystalline compound by evaporation.

The best solvent of cyanide of silver is cyanide of potassium, requiring only one equivalent of the latter to one equivalent of the former, and constituting a distinct compound. This solution, when evaporated, yields an abundant crop of crystals of a mixed character, most generally in the form of hexagonal plates, somewhat resembling chlorate of potash, often intermixed with numerous small crystals, chiefly rhombic prisms, more transparent than the former crystals, which transparency they lose by drying. Their proportion to the other crystals is generally very small. Many crops of crystals are obtained without one of these rhombs being perceptible. Their proportion varies according to the rapidity or slowness of evaporation and variation in the preparation of the salt.

These two forms of crystals were carefully separated and dried at a temperature of 220°. A higher temperature causes the crystals to assume a brownish colour, rendering them exceedingly friable; this condition was therefore cautiously avoided. They were then submitted to the following ana-

lysis:—25 grains were mixed with an equal weight of carbonate of potash and fused; the silver obtained in three different experiments was as follows:—

	I.	II.	III.	Mean
25 grs. of the rhombic prisms gave of silver	12·81	12·88	12·91	12·87
25 grs. of the hexagonal plates ...	13·5	13·38	13·43	13·43

The cyanogen contained in these salts was determined as follows: 25 grains of the crystals were dissolved and saturated with nitrate of silver; the precipitate, washed, dried, and afterwards fused with carbonate of potash, gave of silver:—

	I.	II.	III.	
From the rhombic prisms . . .	25·80	25·55	25·7	Mean 25·68
From the hexagonal crystals . .	26·55	26·63	26·65	Mean 26·61

The mean of these results corresponds with 26·00 of cyanogen in the hexagonal crystals, and 25·08 in the rhombs.

The amount of potassium was not determined by experiment, but calculated from the above results; but from the fact that a solution of the crystals had not the slightest effect upon test papers, proves the absence of free potash; and the precipitate formed by the addition of nitrate of silver to a solution of the salt not being effected by nitric acid, proved that all the potassium in the salt existed as a cyanide.

The results of these analyses in the 100 parts are—

Hexagonal Plates.	Silver .	53·72	Calculated without water.	Silver .	54·02
	Cyanogen	26·00		Cyanogen	26·40
	Potassium	19·28		Potassium	19·58
		99·00			100·00
Rhombs.	Silver .	51·48	Calculated with water.	Silver .	51·69
	Cyanogen	25·08		Cyanogen	25·27
	Potassium	18·59		Potassium	18·70
		95·15		Water .	4·34
					100·00

The water in these crystals was not ascertained by experiment, as it seems to be retained up to the point of decomposition, when cyanogen is also evolved; but these results correspond so closely with those calculated, that we have no hesitation in giving the formula of the one as CyAg + CyK, and the other as CyAg + CyK + HO.

These crystals possess similar properties in every other respect, and may afterwards be spoken of as one salt. They are soluble in 8 parts of cold and in an equal weight of boiling water; are soluble in boiling alcohol, but are deposited again by cooling; they do not deliquesce in the air; their solution does not affect test papers, has a sweet taste when first taken into the mouth, but becomes disagreeably bitter, and the sensa-

tion is not easily removed; it may be boiled for any length of time without decomposition.

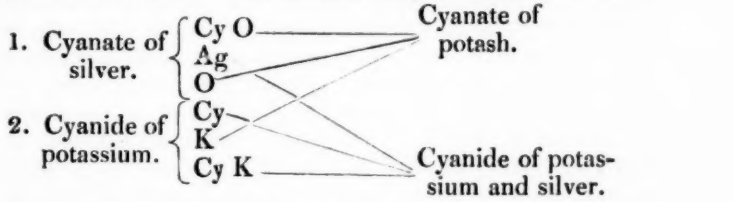
The crystals are easily affected by light, the solution very little so; but a piece of paper dipped into it and dried is very sensitive to light, and would, in our opinion, be a superior salt for photogenic processes to any at present in use. We may also observe here that the analogous salt of gold is ex cellently adapted for the same purposes.

Cyanide of potassium and silver is decomposed by all acids, precipitating the silver as a cyanide; the hydracids however decompose the cyanide of silver also.

Sulphuretted hydrogen precipitates the silver from solutions of cyanide of potassium and silver as a sulphuret. A solution of the salt is not effected by alkaline or earthy chlorides, nor by carbonates.

Perchloride of mercury gives	a white precipitate.
Protosalts of iron	a brownish-white ...
Persalts of iron	a brownish-yellow ...
Lead, nitrate and acetate . . .	a white ...
Protosalts of tin	a yellowish-white ...
Copper salts	a light green ...
Sulphate of zinc	a white ...
Gold	a yellowish-white ...
Nitrate and chloride of cobalt .	a pink, passing to a light violet.
Manganese sulphate	no precipitate.

In the last paper we referred to the superior affinity of cyanogen for silver in the presence of cyanide of potassium, decomposing every salt of silver but the sulphuret, to form cyanide of potassium and silver. As, for example, if cyanide of potassium is added to cyanate of silver, the latter is decomposed by 2 equivalents of cyanide of potassium, and there is produced one of cyanide of potassium and silver with one of cyanate of potash. The reaction may be expressed thus:



A similar reaction takes place when cyanide of potassium is added to the oxide of silver, carbonate of silver or chloride of silver. It is mentioned in Prof. Graham's 'Elements of Chemistry,' upon the authority of Prof. Liebig, that the chloride of silver is soluble in cyanide of potassium, and that

the solution yields a double salt by evaporation. We have repeatedly tried to obtain this double salt, but cannot say we have been successful; it requires two equivalents of cyanide of potassium to obtain the chloride apparently in solution, which then contains chloride of potassium and cyanide of potassium and silver: by repeated crystallization and taking the first crop, we get the latter salt free from the former, which was determined by dissolving some of the crystals thus purified in water and saturating the solution with nitrate of silver. The precipitate being afterwards boiled in sulphuric acid, as noticed in a former part of the present paper, the whole precipitate was dissolved, which would not have occurred had any chloride been present.

It is upon this superior power of silver to combine with cyanide of potassium to form the double salt just described, that we have adopted the method of determining the per-centage of cyanide of potassium in any sample. Nitrate of silver is dissolved in distilled water to such a strength, that two graduations of a common alkalimeter will contain exactly 1 grain of nitrate of silver; 25 grains of the sample to be tried are dissolved, and this solution of nitrate of silver is added cautiously until the precipitate formed ceases to be redissolved; the number of graduations of the silver solution taken are noted, and calculated according to the following equation:—as 170 is to 65·5 so is the number of graduations taken, to the answer, which must be multiplied by 4 to obtain the per-centage. Nitrate of silver of any strength may be used without a graduated measure, but the solution must in that case be evaporated to dryness, treated with hydrochloric acid, again evaporated to dryness, and fused to know the quantity of silver taken; the amount of cyanide of potassium may be known by the following calculation:—As 108·0 is to 131·08 (2 equivalents of cyanide of potassium), so is the weight of silver obtained multiplied by 4 to the per-centage of cyanide of potassium in the sample.

The substitution of cyanide of potassium for any other substance which may be in union with silver is beautifully shown by adding cyanide of potassium to ferrocyanide of silver: it requires 4 equivalents of the former to 1 of the latter to produce 2 equivalents of cyanide of potassium and silver, and 1 of ferrocyanide of potassium; the solution being evaporated the two salts crystallize distinct, and may be easily separated both by their shape and colour. In some experiments of this kind we have been able to recover within one per cent. of the whole of the ferrocyanide of potassium originally used in precipitating the silver.

When cyanide of potassium is added to the ferridcyanide

of silver a similar substitution takes place, requiring 6 equivalents of cyanide of potassium to get the whole into solution; but the primary action is somewhat different in this salt from any other we have tried. When cyanide of potassium is added to ferrocyanide of silver, the formation of the double salt of silver and potassium, and the ferrocyanide of potassium, are simultaneous; and if there be not 4 equivalents of cyanide of potassium added, the remaining precipitate is undecomposed ferrocyanide of silver. But on adding cyanide of potassium to the ferridcyanide of silver, the first action is the decomposition of the whole ferridcyanide of silver, with the formation of cyanide of silver and ferridcyanide of potassium; 3 equivalents of cyanide of potassium effect this change, the precipitates passing from an orange to a white; the ferridcyanide of potassium may be decanted from the precipitate without having any silver in solution. Several other interesting reactions take place with these substances, which have not yet been sufficiently investigated to be brought forward. In conclusion, however, we may mention a reaction with the ferrocyanides of the metals, which, so far as we are aware, has not yet been observed in any chemical work; it is that the ferrocyanides of the metals are converted into the ferridcyanides by adding an excess of nitric acid to these compounds; if, for example, we add nitric acid to the ferrocyanide of silver, it is immediately changed from a white to a deep orange; 1 equivalent of silver is dissolved, and every 2 equivalents of ferrocyanide of silver with nitric acid produces one of nitrate silver and one of ferridcyanide of silver.

When the ferridcyanide of silver is heated in water to about 150°, it loses its orange colour and becomes green, which colour is permanent; any acid or nitrate of silver present prevents this change until the precipitate is dried and heated. This green precipitate has not yet been examined. It can be obtained either with the ferridcyanide formed by the nitric acid upon ferrocyanide, or by precipitating silver with ferridcyanide of potassium.

March 18, 1844.—Richard Phillips, Esq., V.P., in the Chair.

John Lee, Esq., and Mons. F. C. Calvert were elected Members of the Society.

The following communications were then read:—

C. *On the occurrence of Fluorine in Recent as well as in Fossil Bones.* *By* Charles Daubeny, *M.D., F.R.S.*

HAVING in the course of the preceding spring paid a visit to the deposit of compact phosphorite which occurs in the province of Estremadura in Spain, I was subsequently

led to examine into the chemical constitution of the mineral which forms the prevailing ingredient of the vein to which my inquiries had been directed.

The results of my examination have already been reported in the memoir communicated by my fellow-traveller Captain Widdrington, R.N. and myself to the Geological Society with respect to the rock in question, and read at their meeting on the 17th of January last; from which it will be seen, that the mineral, although, not being crystallized, it is somewhat variable in its composition, yet when selected as pure as possible, contains as much as 81 per cent. of phosphate of lime, and 14 per cent. of fluoride of calcium, the remainder appearing to consist of silica and peroxide of iron*.

The conclusion arrived at with respect to the compact form of mineral phosphate of lime occurring in the above locality, coupled with the reports of other chemists to the same effect relative to crystallized apatite, naturally led me to speculate as to the final causes of the apparently constant association of fluoride of calcium with earthy phosphates amongst the older materials of the globe, and to ask myself, whether it might not be possible, that fluorine, as well as phosphorus, fulfilled some hitherto unexplained office, in the œconomy of those organic beings, for the sake of which such mineral matters may

* The phosphate of lime I have since satisfied myself to possess the same composition as apatite, viz. PO_5+3CaO; and this is confirmed by Mr. Middleton and Mr. D. Campbell, in the laboratory of Professor Graham, who were kind enough each to undertake an independent analysis of the mineral. They likewise agree with me, and with each other, in their estimation of the amount of fluoride of calcium, determined by the loss occasioned on the addition of sulphuric acid to the pounded specimen, from which loss the proportion of fluorine was calculated. I should however remark that this quantity is double that of the largest amount reported by Rose to be present in the crystallized apatites which he examined (see Thomson's Mineralogy, vol. i. p. 125); and that I have never succeeded in obtaining more than 8·8 grains per cent. of fluoride of calcium by the direct method, in which the fluorine was expelled by heat and sulphuric acid from the phosphorite contained in a platina still, and where, after passing it through a silver vessel kept at 500°, in which any earthy matter carried over with the vapour might be deposited, it was finally received into a glass vessel containing caustic ammonia. As sulphate and fluate of ammonia could alone be formed, I estimated the amount of fluorine by adding chloride of calcium, and separating the resulting sulphate of lime from the fluoride of calcium by repeated washings with water. I apprehend, however, that in this method the whole of the fluorine may not have been driven over, in spite of all the pains bestowed upon the process.

I am desirous of appending the analysis given by Messrs. Middleton and Campbell of the mineral, as though they differ, as might be expected, somewhat from my own in the entire quantity of phosphate of lime present in the specimens they examined, they confirm nevertheless my statement as to the relation both between the phosphoric acid and the lime, and between the phosphate of lime and fluoride of calcium present.

The portion examined by Mr. Middleton was in the form of a brown

be conjectured to have been treasured up in the rock formations from the beginning of time.

These reflections brought to my mind the researches of Morichini and of Berzelius with respect to the existence of fluorine in bones, seeing that the latter, according to the concurrent testimony of both these philosophers, appear to contain as a constant ingredient a minute quantity of fluoride of calcium, inasmuch as its presence is vouched for by them, in recent as well as in fossil bones, and in the teeth of mammalia, as well as in other parts of their osseous structure.

Here however I was compelled to pause, by observing the contrary statements put forth by other able chemists relative to this point; Fourcroy and Vauquelin having, previously to the researches of Berzelius, denied the existence of fluorine in recent bones, and Dr. Rees having, subsequently to them, in a memoir drawn up under a full knowledge of what had been done before, arrived at a conclusion equally opposed to that of the Swedish philosopher; one too which has been since corroborated in a communication relative to the composition of bones made to the French Institute by Messrs. Girardin and Preisser of Rouen, and lately published in the *Comptes Rendus*.

As however none of these gentlemen appear to dispute that fluorine does occur *in fossil bones* generally, the conclusion

earth, containing nodules of a pure white, corresponding probably with the original condition of the formation generally. The results of analysis were as follow:—

Phosphate of lime	73·66
Fluoride of calcium	15·10
Phosphate of iron	4·26
Peroxide of iron	1·16
Matter insoluble in acids	3·95
Loss on heating to low redness after thorough drying	·78
Loss in the process	1·09
	100·00

The constitution of the phosphate seems to be $CaF + 2\,(3CaO\,PO_5)$.

Analysis by Mr. Campbell.

1. 6·89 grains of a mixed substance, as received from Dr. Daubeny:—

Phosphate of lime ($3CaO\,PO_5$)	4·78 =	69·38
Phosphate of iron	·70 =	10·16
Fluoride of calcium	1·01 =	14·66
Peroxide of iron	·02 =	·29
Insoluble matter in acids	·38 =	5·51
	6·89 =	100·00

2. Analysis of white crystalline solid mass; 11·00 grains gave,—

Phosphate of lime ($3CaO\,PO_5$)	8·68 =	78·90
Fluoride of calcium	·63 =	14·82
Matter insoluble in acids	·66 =	6·00
Loss in experiment	·03 =	·28
	11·00 =	100·00

they have arrived at leaves the subject, it must be confessed, encumbered with greater difficulties than before, for as all sound chemical analogies stand opposed to the admission of the idea, that fluorine can have been generated from the other constituents, during any process of decay or alteration that might have occurred in it, during the ages that had elapsed since it formed a part of the living structure, we should be driven to the belief, that the fluoride of calcium contained in bone had filtered in from without,—a conjecture which, although perfectly plausible, if the occurrence of this ingredient had been casual, or had been limited to bones found in rocks of a certain age or composition, seemed rather a violent one, when extended to those of all ages and formations, being scarcely reconcileable with the rarity of the mineral itself in the waters of springs, and its sparing solubility in most reagents.

These difficulties that occurred to my mind, no less than the weight I attached to the positive testimony of the great Swedish chemist in favour of the existence of fluorine in recent bones, induced me to consider, whether it might not be possible that certain circumstances had operated in the mode of conducting the experiment, by which the presence of fluorine in the hands of the chemists who adopt the opposite conclusion escaped detection.

And on further investigation it appeared to me, that two ingredients naturally present in recent bones might have interfered with the result in the instances alluded to.

The first of these is animal matter, which, owing to the strong affinity it possesses for fluorine, may arrest its escape, and thus prevent it from coming into contact with the glass.

The second, salts containing any volatilizable ingredient, such as the carbonic or muriatic acids, which would be disengaged by the same agent by which the fluorine was set at liberty, and which, escaping in a rapid current, might carry the latter along with them, before it could have time to exert any sensible action upon the glass suspended over it. Accordingly I found, that whilst one-tenth of a grain of fluor spar mixed with more than 100 grains of any earthy mineral, occasioned under the action of sulphuric acid an easily discernible, though faint corrosion on the exposed parts of the glass, the same quantity produced no effect whatever, when mixed with 5 per cent. of carbonate of lime, or with a little gelatine; and that half a grain of fluor spar and the earth, when mixed with gelatine, caused a trace on glass not much more distinct than that occasioned by one-tenth of a grain without this admixture.

In testing, therefore, the bones and teeth which I had obtained for examination, I did not choose to content myself with merely adding sulphuric acid to the pulverized specimen, but I began by burning off all the animal matter; and then, finding that the carbonic acid still in part remained, I dissolved the earthy residuum in muriatic acid, and threw down by means of caustic ammonia the earthy phosphates.

The latter, after being well washed and dried, were treated with concentrated sulphuric acid in a platina crucible, covered over by a plate of glass, shielded, except on the parts intended to be acted upon, by a coating of wax, but no artificial heat was applied, as the sulphuric acid, by its action upon the phosphate, raised the temperature sufficiently to expel whatever fluoric acid might be present in the specimen.

The glass was allowed to remain as a cover to the platina crucible for at least two hours, and in order to ensure the condensation upon it of the hydrofluoric vapour, a rim of wax was placed round the margin of the upper surface of the glass, by means of which a small portion of water might be kept the whole time in contact with it, so as to maintain a suitably low temperature.

That these precautions were not unnecessary I satisfied myself, by observing the difference in the degree of corrosion produced by a fossil bone given me by Dr. Buckland from the cave of Kirkdale in Yorkshire, when thus purified from the animal matter of which its long interment had not yet deprived it, as well as of its carbonic acid, as compared with the same, when treated with sulphuric acid without having undergone such a preparation.

In proof of this I submit to the inspection of members specimens No. 3 and No. 4; the one showing the glass corroded by a Kirkdale bone deprived of its animal matter and carbonic acid; the latter, by one retaining both. Operating in this manner, I have succeeded in engraving upon glass, not only by means of fossil bones, from Stonesfield, from Montmartre, from the cave of Kirkdale in Yorkshire, and from that of Gailenreuth in Franconia, specimens of all which were supplied me by Dr. Buckland; but likewise with the bone of some quadruped that had been lying for a long, but unknown time, exposed to the weather in the soil of our Botanic Garden; with the vertebra of an ox recently killed; with the tibia of a human subject from an anatomical cabinet at Oxford; with the teeth of an ox just killed, and with human teeth of recent date. The markings differ widely in the degree of their distinctness, and are in some instances so faint as hardly to be discerned except by daylight; but I have

convinced myself that they cannot be attributed to the disengagement of phosphoric acid, as the same glass was in no degree affected by the fumes proceeding from the action of sulphuric acid upon pure phosphate of lime, where the acid had been derived from the direct combustion of phosphorus, nor, for a long time at least, by the vapour of free phosphoric acid exposed to a heat sufficiently great to fuse and partially to volatilize it.

Nor was it dependent on any peculiarity in the nature of the glass, for plate glass was corroded in the same manner as the crown glass more usually employed.

By the oldest and most fossilized specimens the glass seemed undoubtedly to be most deeply etched; yet even here there occurred exceptions, for the marks caused by a bear's bone taken from Gailenreuth are the faintest in the whole series, and were produced only after a long exposure to the acid vapours, two previous trials having proved unsuccessful; whilst, on the other hand, the tibia of a human subject gave indications almost as distinct as any even of the fossil bones operated upon.

It would doubtless have been more satisfactory if I could have stated the proportion of fluorine in these samples of bones and teeth, as well as the fact of its actual presence, and likewise if I had extended my examination over a larger number of specimens; but I have been compelled to postpone the former part of the inquiry until I could obtain an apparatus suitable for the purpose, and doubted when my time would permit me to carry further the present investigation, if, in order to give my results in a state of greater completeness, I neglected the present opportunity of communicating them*. The only criterion, therefore, I am at present enabled to offer as to the proportion of fluorine in the bones examined, is a comparison of the depth and distinctness of the marks produced by the latter, with those caused by a certain known amount of fluor spar, mixed with a weight of phosphate of lime or other earthy material equal to that present in the bones operated upon. Judging by this rough mode of measurement, it would appear, that in several instances the faintness of the marks shows a smaller quantity of fluorine to have been present in the specimen, than would have been contained in a

* I have since, by the aid of the apparatus described in the former note, attempted to estimate the amount of fluorine in the fossil bone from Stonesfield, and in the recent human bone from an anatomical cabinet. The former afforded 8·7 grains per cent. of fluoride of calcium, the latter only 2·0, results which will at least indicate the *relative*, if not the *absolute* quantity of fluorine present.

mixture of one-tenth of a grain of fluor spar added to 100 grains of phosphate of lime.

The existence of fluoric acid, as a constant, or at least a common ingredient in bones of all ages, would seem *à priori* to be much more probable, than its absence in recent bones would be, if its normal presence in fossil ones be admitted, for we can readily understand its finding its way into the animal structure through the medium of plants, which may imbibe it along with those phosphates with which it is so generally associated. Indeed it seems so likely, that those vegetables at least that contain much phosphate of lime should possess a trace of it, that I am at this very time examining the ashes of barley with reference to the latter point*.

The greater distinctness of the marks produced by the fossil bones acted upon than by the recent ones may be more difficult of explanation; but before it is urged as an objection against the view taken, it should be determined, whether the difference may not arise from the removal of the greater part of the animal matter from the fossil bone, owing to its long interment in the earth. Of the six specimens of fossil and recent bones of which I made a rough analysis, that from Stonesfield, which was the oldest of any, having been imbedded in a secondary rock belonging to the oolite formation, lost, by exposure to a heat of 212°, 4·2 per cent.; by a further heat of about 500°, 5·0 per cent. more, and by increasing the temperature to a red heat only 1·8 per cent. in addition, the latter probably representing very nearly the amount of animal matter remaining, the two former numbers the water retained within the bone.

Proceeding upon the same data, the bone from the tertiary rocks of the Paris basin, next in the order of antiquity, would contain 10 per cent. of water, 2 of animal matter. The bone from Gailenreuth, water 13·9, animal matter 5·0; that from Kirkdale 12·5 water, 11 animal matter; whereas the recent bone picked up in the Botanic Garden contained, even when dry externally, about 30 per cent. of water and 11 animal matter; and the human tibia, which had been kept in an anatomical cabinet for a certain time, gave out 23 per cent. of water and 17 of animal matter.

It may also be suggested, as a possible explanation, that the

* I have since ascertained that no sensible action is exerted on glass by heating with sulphuric acid the earthy phosphates present in 12 lbs. of barley. Sprengel, I find, had already suggested the probable occurrence of fluorine in plants, but conceives that it exists in such a state of combination, as causes it to be dissipated by the heat necessary for expelling the carbonaceous matter, and therefore cannot be detected in the ordinary method.

fluoride of calcium distributed through the mass has in the course of time become collected into little nuclei in certain parts of the bone, and for this reason may allow of a more ready disengagement from it of the fluoric acid which it contains as an ingredient.

That a certain alteration in the arrangement of the earthy particles of a bone does occasionally take place after its deposition, is evidenced from the curious observations by Messrs. Girardin and Preisser, in the memoir which has been already referred to, as these gentlemen state, that the bone-earth phosphate appears in some instances to have separated into two distinct compounds, crystals of apatite being recognised by them in some of the fossil bones in their possession, which they conceive to have arisen from the segregation of the tribasic from the bibasic compound.

Will not this latter fact also help us towards an understanding of the function which fluate of lime may fulfil in the structure of bones, and likewise of the peculiar adaptation of the bone-earth phosphate to serve as its prevailing earthy ingredient?

It seems a general law in both kingdoms of organic nature, that crystallization should operate as a sort of antagonist force to the processes of assimilation, so that no material can be fitted to enter into the fabric of a living body, between whose particles the natural force of polarity operates with all its energy. Hence, according to Dr. Prout, the use of the infinitesimal portions of foreign inorganic matter interposed between the particles of most bodies which form the constituents of vegetable or animal organization; and although it may be true, as has been suggested by Von Buch, that the very prismatic form which belongs to phosphate of lime as a mineral species, adapts it for the fibrous structure of bone better than other earthy compounds in which the axis of crystallization is equal in both directions, yet even in this case the tendency to arrange itself according to the laws which regulate inert matter might operate too powerfully, were it not diminished by the association in equal atomic weights of the two phosphates, each of which possesses a polarity in some degree differing from the other, and consequently to a certain extent counteracts the disposition in the particles of the other to assume a determinate arrangement.

If there be any truth in these speculations, is it not also conceivable, that the interposition of a mineral matter, like fluor spar, whose particles crystallize in quite another manner, that is in cubes, may cooperate on the same principle, in imparting that freedom of motion to the particles of the prevailing

constituent of bones, by which it is rendered more pliant to the purposes of the animal economy, more obedient to the laws of life, more ready in short to insinuate itself into the pores, so as to form the coats of those delicate capillary canals of which the osseous structure appears to consist?

CI. *On a Spathic Carbonate of Iron.*

By Mr. John Thomas Way.

THE mineral which forms the subject of the present notice was put into my hands by Professor Graham. It would seem that its appearance had caused it to be mistaken for zinc blende, which indeed it somewhat resembles in its colour and lustre. Upon examination however it was found to contain no zinc, but to be essentially a carbonate of the protoxide of iron with hydrated peroxide of iron.

The mineral is massive, of a brownish-black colour, pretty compact structure, and exhibiting, when broken, crystalline, generally rhomboidal and curved facets of a somewhat pearly lustre. It is not homogeneous, some portions of it, when crushed in an agate mortar, giving a powder of a much whiter colour than others; none of it is magnetic.

Its specific gravity is 3·747.

This mineral yields nothing to water, but (with the exception of a mere trace of silica) is entirely soluble with effervescence in acids. Nitric and sulphuric acids dissolve it in the cold, but more readily with the assistance of heat. Hydrochloric acid appears to act upon it with more energy than either sulphuric or nitric acid.

When analysed, the mineral was found to contain carbonic acid, protoxide and peroxide of iron, lime and water.

In order to obtain it as homogeneous as possible for quantitative analysis, considerable portions of the mineral, which is not harder than marble, were reduced to powder and well mixed.

The results of two analyses subjoined, however, show that its composition is not quite uniform.

	I.	II.	Mean.
Carbonic acid . . .	36·13	36·03	36·08
Protoxide of iron . .	51·33	50·18	50·75
Peroxide of iron . .	8·26	9·60	8·93
Lime	4·75	3·74	4·24
Water	1·02	1·14	1·08
	101·49	100·69	101·08

The excess in the analyses appears to be due to an imper-

fect mixture of the different parts of the mineral, several portions having been taken for the various operations.

The water is as nearly as possible in the proportion to form protohydrate of the peroxide ($Fe_2O_3 + HO$), and there is little doubt exists in that condition.

The composition of the mineral may therefore be thus expressed:—

Carbonate of protoxide of iron . .	83·60
Carbonate of lime	7·47
Hydrated peroxide of iron	10·01
	101·08

In examining the composition of this substance, considered as a variety of the spathic carbonate of iron, the first peculiarity worthy of attention is the absence of manganese.

It would appear from all recorded analyses of the spathic carbonate of iron, and also of carbonate of iron as existing in clay-iron-stone, that manganese is a usual ingredient of both varieties. Dr. Thomson of Glasgow describes, in his 'Outlines of Mineralogy,' a brown mineral under the name of "Hydrous Carbonate of Iron," which appears from the analysis he supplies to be of similar constitution to that under notice,—consisting of carbonate of the protoxide of iron with hydrated peroxide of iron, but differing in containing so much as 4·75 per cent. of protoxide of manganese.

In four out of eight analyses by Dr. Colquhoun of clay-iron-stone from the coal beds in the neighbourhood of Glasgow, given in the same work, manganese is mentioned, although in much smaller quantity; and the analyses by Berthier of nineteen varieties of iron ore from the coal beds of France exhibit the uniform presence of the oxide of this metal in a proportion varying from 0·5 to 4 per cent.

The absence of manganese is perhaps, however, less interesting in a scientific than in an œconomical point of view, and can easily be conceived in a crystallized mineral, which appears to have undergone so little alteration.

Its freedom from silica (with the exception of a mere trace not mentioned in the analyses, and existing as grains of quartz and not in combination), from alumina, magnesia and phosphoric acid, are also matters more affecting the value of this ore as a source of iron than its interest as a subject of scientific inquiry.

The action of acids upon the mineral is peculiar, and throws some light on its constitution and the probable circumstances of its formation. When treated in the state of fine powder with diluted hydrochloric acid it is gradually dissolved with effervescence, but the action is by no means rapid; if heat be

applied considerably more effect is produced, but not such as we are accustomed to witness in the solution of carbonates.

If the acid be poured off after a short digestion with heat upon the powdered mineral, the residue undissolved is in the state of a white crystalline powder, which dissolves very slowly even in concentrated, and scarcely at all in dilute mineral or in vegetable acids.

Upon examination, this crystalline carbonate was seen under the microscope to consist of well-defined perfectly transparent crystals, having the rhomboidal form of calc spar. Notwithstanding the prolonged action of acids to which the mineral had been subjected, the crystals were found to retain a considerable quantity of lime. It was thought advisable therefore to subject the substance to analysis. The result was:—

Protoxide of iron	56·14
Carbonic acid	39·03
Lime	5·04
	100·21

Its composition is therefore

Carbonate of protoxide of iron .	91·24
Carbonate of lime.	8·97
	100·21

It will be seen that the carbonate of lime is here in larger proportion than in the original mineral, which should be the case if the digestion in acids removes only or principally the peroxide of iron.

There can be little doubt that the deposition of carbonate of lime had occurred in the crystals simultaneously with that of carbonate of iron, a circumstance of easy explanation from the isomorphous relations of iron and lime in their carbonates.

The simplest method of dissolving up the peroxide of iron so as to obtain this pure carbonate of iron, appears to be to digest the powdered mineral in strong hydrochloric acid till all the black matter is removed, which occurs in a few minutes, to wash and dry by a heat of 212°.

The power which carbonate of iron in this state opposes to the action of acids is well illustrated in another instance, in which masses of the size of split peas were introduced into commercial hydrochloric acid diluted with an equal bulk of water, a state most favourable to the solution of a carbonate. After digestion for a night, the acid remaining in excess, the carbonate was found undissolved, the only effect being the removal in solution of the hydrated peroxide and consequent disintegration of the mineral. Some of the carbonate had undoubtedly dissolved, but the greater part escaped.

This separation of the constituents of the substance under

examination is a very distinct denial to the supposition that they exist in a state of combination, and indicates at the same time a very considerable resistance to external agencies. It comes then to be an interesting mineralogical inquiry in what way the peroxide of iron found its way into the mineral. In the description of the "hydrous carbonate of iron," Dr. Thomson states his belief that the peroxide had originally existed in the state of carbonate of the protoxide, but that by exposure to the weather this had lost carbonic acid and become peroxide.

I might perhaps be allowed to go a step further, and suggest the possibility that some of the lime which exists in the mineral might, in solution in carbonic acid water, have penetrated it by infiltration, and that the excess of carbonic acid would dissolve the carbonate of iron, and afterwards, upon evaporation, leave it exposed as hydrated carbonate—a state most favourable to atmospheric agency.

The value of this mineral, however, in an œconomical point of view, constitutes unquestionably its chief interest, and on this part of the subject it is to be regretted that only vague information can be afforded.

The mineral came from Hull; the only information that accompanied it is, that "it forms a vein of from 4 to 10 fathoms in thickness by upwards of 100 fathoms in width, within about 15 miles of coal and railway." This of course would afford an enormous supply.

By the analysis it will be observed that the total amount of iron as carbonate and peroxide is equivalent to about 45 per cent. Comparing this with Mushet's black band (the richest ore which is worked in England), we have, it is true, no great preponderance in favour of the spathic carbonate, except in the purity of the ore. In comparison, however, with the ores usually employed in this country it possesses great advantages.

Of 7 analyses of clay iron-stone from the Glasgow fields the average in iron is 30 per cent.; showing an advantage of 50 per cent. on the product to be obtained from this mineral.

This, although a vast recommendation, is perhaps the least that can be urged in favour of this valuable ore. The ease with which it would be worked is another subject of considerable importance. A simple reduction with carbonaceous matter is probably all that would be required, there being little or no impurities which would call for a flux to remove them.

But the remarkable purity of the mineral is that which as a source of iron would principally constitute its value, and would fit it eminently for the production of the best varieties of that substance, and would enable it to rival successfully the Swedish ore in this especial application of iron.

I regret exceedingly my inability to supply more tangible information as to the extent and locality of this ore, and its relations to the coal strata, which must materially affect its value; but repeated attempts to obtain this information have proved abortive, I presume, from the existence of a jealousy on the part of the proprietors to divulge it.

It is well however that the attention of mineralogists should be drawn to the subject, as it is by no means improbable that spathic iron ore may exist in other localities to an equally large extent.

March 30, 1844.—Anniversary Meeting.—The President in the Chair.

The following Report of the Council was read from the Chair, and subsequently ordered to be printed in the Society's Transactions:—

THE experience of the present year confirms the favourable anticipations expressed at the last Anniversary respecting the stability of the Chemical Society. The exertions made on the first foundation of any society are evidence of little more than the meritorious zeal and activity of the few with whom it has originated, and are in their very nature extraordinary and temporary. It is only when these exertions begin to subside to their usual level, and the welfare of the Society, then necessarily entrusted to the voluntary efforts of the members at large, is found to have received no check, that expectations can reasonably be entertained of the final success of the undertaking. Our Society may, I think, be now fairly considered as passing through this critical state of transition, while it exhibits at the same time signs of such healthy vigour as may well encourage us to perseverance in the good work. Our periodical meetings have been fully attended during the present session, and the number of those whom the various accidents of civil society have removed from our last year's list of members have been more than replaced by the new elections. We have added to our list 8 resident and 12 non-resident members, 1 foreign member and 6 associates, being 27 in the whole; the entire number on our list is 168, of which 78 resident and 71 non-resident members contribute to our finances the sum of £227. From our 4 foreign members and 15 associates, though no pecuniary supplies are expected, we look with confidence to communications which may be alike worthy of them to offer and of the Society to receive.

The Society has to regret the loss by death of one of its members, Mr. Charles Macintosh, with whose name every one is familiar, and who will long hold a place in the memory of his personal friends. This gentleman was the son of George

Macintosh, a merchant of Glasgow, who first introduced into Scotland the process of dying Turkey red. After going through the usual routine of a school education he was placed while young in a merchant's counting-house at Glasgow. A strong bent to science induced him to enter himself as a student in the University of his native place, where for several sessions he attended the lectures of Dr. Black and afterwards of Dr. Irvine, the successor of Dr. Black, on the removal of the latter to the Chemical Professorship in the University of Edinburgh. He next spent some time in France, and thus acquired a familiar use of the French language.

On his return to Glasgow he established himself as a chemical manufacturer, chiefly of salts and other substances used in dyeing, bleaching and calico printing, and is stated to have have been the inventor of the method of preparing the dry chloride of lime.

The last important object in which he was engaged was a project for rendering cloth water-proof by interposing between two webs of cloth a thin layer of a solution of caoutchouc. By great care and attention he succeeded in improving this process from time to time, and ultimately brought it to its present state of perfection.

It does not appear that he contributed in any marked degree to the advancement of scientific chemistry, but he may be considered as holding a high place among those whose sagacity and practical talents have aided the progress of manufacturing industry, and have received accordingly their appropriate reward. He died on the 25th July, 1843.

The arrangement by which, on the payment of a moderate rent, we are accommodated with rooms for our use at the house of the Society of Arts continues to be satisfactory to both parties, and especially to ourselves, as we have not only acquired a convenient habitation, but have avoided those expenses included in the word establishment so often ruinous to young societies.

Parts 5 and 6 of the Memoirs and Proceedings of the Society have been distributed to the Members, and Part 7 is on the point of being issued. The two former contain fourteen papers read since our last anniversary, several of which are of high interest, both theoretically and practically. Among these I may perhaps be allowed to point out Mr. Denham Smith's examination of the basic sulphates of copper; Mr. Stenhouse's determination of the atomic composition of pure theine; and an inquiry by Mr. Warington and Mr. Francis on the action of alkalies on bees' wax, showing that the fatty body contained in this substance is not stearine, a fact of some importance in reference to the controversy be-

tween Liebig and certain French chemists respecting the source of the fat in animal bodies. Of the importance of Dr. W. Gregory's paper, entitled 'Further contributions to the chemical history of the products of the decomposition of uric acid,' there can be but one opinion. In a short memoir this accomplished chemist, commencing from the mother-liquid of alloxan, makes known the methods of preparing alloxantine, dialuric acid and dialurate of ammonia, the composition of the second of which he found on actual analysis to correspond to the hypothetical formula previously given by Liebig and Wöhler, namely, $C_8 H_4 N_2 O_8 + HO$. He also describes alloxano-sulphurous acid, apparently a new substance, and alloxanic acid. These investigations, in which Dr. Gregory is still occupied, are owing to Professor Liebig having very liberally placed at his disposal a large quantity, above 2 lbs., of urate of ammonia. Of these interesting substances I find from a letter of Dr. Gregory's to our Secretary that specimens will be forwarded for the Society's Museum.

And this leads me to say a few words concerning our Museum, or rather nucleus of a Museum. Among the specimens presented are some from Dr. Stenhouse, illustrative of his paper on the products of the distillation of meconic acid. Such specimens have a double value, not only as samples of new or rare substances, but have the same value as original documents in historical inquiries, as they admit of being referred to in order to correct or corroborate statements made in the Memoirs to which they relate. But while it is recommended that documentary specimens, so to speak, should, when possible, accompany the papers with which we may be favoured, I wish to impress on our Members the utility of the Society possessing as large a collection as possible of known chemical substances in their purest and most characteristic state. To our excellent Secretary, as well as to other Members, we are indebted for several fine specimens received during the present session; and I am sure it only requires that the wish of the Society on this subject should be generally made known among us to bring this part of our collection to a very satisfactory state. Of books and periodical journals, we have received several from the respective authors and editors, which, together with the journals purchased from the funds of the Society, will enable our Members to become acquainted with the discoveries, as they arise, both theoretical and practical, in a science second to none in importance and interest, in the rapidity of its progress, and the boundless extent of discovery which it offers to us and our successors.

The state of the Society's funds will be exhibited by the following audited account of the Treasurer.

AUDITORS' REPORT.

Dr. ROBERT PORRETT, (*Treasurer*) *in Account with the Chemical Society of London.* *Cr.*

		£	s.	d.
1843.				
March 30.	To Balance from last Account	269	15	3
1844.				
March 25.	To Subscriptions since received	193	0	0
		£462	15	3

		£	s.	d.
1843.				
March 30.	By payment for Specimen Bottles	1	16	0
	——— for Duty and Charges on Chemicals from Giessen	1	4	1
May 2.	——— for Scientific Journals for 1843	5	5	0
16.	——— for Rent to Society of Arts	25	0	0
16.	——— for Printing, from Oct. 1841, including the Society's Memoirs and Proceedings	86	19	6
Dec. 18.	——— of Gratuity to Doorkeeper Society of Arts	0	10	0
1844.				
Jan. 15.	——— for Philosophical Magazine and Scientific Memoirs	5	7	0
Feb. 7.	——— for Scientific Journals for 1844	3	15	0
March 23.	——— to Collector for Poundage	7	8	3
23.	——— for Envelopes, Paper and Postage Stamps	3	2	0
25.	By Balance to his Debit in new Account	322	8	5
		£462	15	3

London, 25th March, 1844.

R. PORRETT, *Treasurer.*

We have examined the above Account and find it correct,

B. G. BABINGTON.

PHILIP J. CHABOT.

The following Gentlemen were elected as Officers and Council for the ensuing year:—

President.—Arthur Aikin, Esq.

Vice-Presidents.—William Thomas Brande, Esq.; John Thomas Cooper, Esq.; Thomas Graham, Esq.; Thomas Thomson, M.D.

Treasurer.—Robert Porrett, Esq.

Secretaries.—Robert Warington, Esq. and George Fownes, Ph.D.

Foreign Secretary.—E. F. Teschemacher, Esq.

Council.—Benjamin Babington, M.D.; Thomas Everett, Esq.; M. Faraday, D.C.L.; William Gregory, M.D.; Percival N. Johnson, Esq.; James F. W. Johnstone, Esq., M.A.; H. B. Leeson, M.D.; W. Hallows Miller, Esq., M.A.; William Hasledine Pepys, Esq.; Richard Phillips, Esq.; J. Denham Smith, Esq. and John Stenhouse, Ph.D.

The thanks of the Society were severally voted to the Officers and Council for their exertions during the past year.

April 1, 1844.—The President in the Chair.

The following presents were announced to the Society's Museum:—

Specimens of the Hydrate of Laurel Oil; of the Meconate of Iron and Ammonia and of Komenate of Copper, from Dr. Stenhouse. Fluoride of Iodine, from Dr. Leeson. East Indian Grass Oil, from Dr. Potts; and Four specimens of Crystallized Iron Pyrites, from Mr. Wonfor.

The following communications were then read:—

CII. *On some of the Salts of Meconic and Komenic Acids.* By John Stenhouse, *Ph.D.*

THE meconic acid employed in the following experiments was made by Robiquet's process, as modified by Gregory. The crystallized acid had only a slightly yellowish shade, and when heated on platinum foil it disappeared without leaving any residue When dried at 212° F. it was subjected to analysis. 0·4533 gram. of acid gave 0·696 of carbonic acid and 0·0847 of water.

		Calculated numbers.		
				Per cent.
Carbon	42·45	Carbon	14 =	42·460
Hydrogen	2·07	Hydrogen	1 =	1·979
Oxygen	55·48	Oxygen	11 =	55·561
	100·00			100·000

Meconate of Lead.

When meconic acid is added in slight excess to a solution of neutral acetate of lead, it causes a bulky flocculent precipi-

tate, which is nearly white, with only a slight shade of yellow. The precipitate is insoluble in either hot or cold water. When washed and dried at 212° F. it was subjected to analysis.

	Gram.				Per cent.
I.	0·4707	gave 0·0348	lead and 0·262	oxide	= 63·62
II.	0·420	... 0·0495	... 0·213	...	= 63·41
III.	0·3952	... 0·0543	... 0·1927	...	= 63·56
IV.	0·4508	... 0·0385	... 0·2435	...	= 63·21
V.	0·4987	... 0·1043	... 0·203	...	= 63·23

I. 0·367 grm. of salt ignited with chromate of lead gave 0·215 of carbonic acid and 0·0211 of water.

II. 0·554 grm. gave 0·331 of carbonic acid and 0·0346 of water.

	I.	II.	At.	Calculated numbers.		Per cent.
C	=16·19	16·52	14	Carbon	=1070·09	16·23
H	= ·63	·69	3	Hydrogen	= 37·44	·57
O	=19·78	19·39	13	Oxygen	=1300·00	19·72
PbO	=63·40	63·40	3	PbO	=4183·5	63·48
	100·00	100·00			6591·03	100·00

The salt employed in these determinations was made at three different times; that used for the first and second determinations was washed with hot water, the others were washed with cold water. The salt is evidently tribasic with 2 atoms water, and its formula is consequently $\overline{Me} + 3PbO + 2aq$. I have been quite unable to obtain Robiquet's salt: $\overline{Me} + 2PbO + aq$.

When meconate of ammonia is added to a solution of acetate of lead, rendered also slightly alkaline by ammonia, still more basic salts are formed. They fall as deep yellow insoluble precipitates. In the course of three trials I was quite unable to procure them of definite composition. The mean of several determinations of one quantity gave 68·38 per cent. oxide of lead, a second gave 74·76, and a third 71·07 per cent. The first quantity was washed with hot, and the other two with cold water.

Meconic Acid and the Persalts of Iron.

When meconic acid is added to a solution of any of the persalts of iron, the liquid, as is well known, immediately assumes a blood-red colour; but even though very concentrated it may be kept for any length of time without its giving any precipitate. With an alcoholic solution of meconic acid the result is precisely similar.

If, however, a tolerably concentrated aqueous solution of

meconic acid is first neutralized with ammonia, and then treated with a slight excess of very neutral persulphate of iron, after standing for a few hours a fine bright crimson precipitate appears in considerable quantity. This powder, which is not at all crystalline, should be collected on a filter and washed with cold water till the liquid which passes off is but slightly coloured, and ceases to give any indication of containing sulphuric acid. The red precipitate is not very soluble in cold water or alcohol, but dissolves very readily either in an acid solution or in hot water. When its solution is treated with potash or soda it is instantly rendered colourless, and the smell of ammonia becomes very perceptible. The iron is precipitated in reddish flocks, evidently in the state of peroxide, for when redissolved in muriatic acid, and tested with red prussiate of potash, not the slightest blue tint is perceptible.

If a solution of the powder which has been decolorized by potash be cautiously neutralized by muriatic acid, the red colour reappears, but is destroyed by the addition of more acid. The iron is not precipitated by ammonia, even when added in great excess, and the colour is only changed from a blood-red to a deep reddish yellow. Hydrate of lime also destroys the colour, precipitates the iron as peroxide and evolves ammonia. If the red powder is dried at an ordinary temperature it retains its bright colour, but if it is heated as high as 212° F. it becomes reddish brown, losing its lustre. If first dried at an ordinary temperature, it may be heated as high as 212° F. without any reduction of its oxide. But if its solution is kept for some time at 120° F., it is partially reduced; and if boiled for an hour or so its red colour disappears, and the peroxide of iron it contains is wholly reduced to the state of protoxide. When dried at 212° F., and subjected to analysis, the determinations of the iron double salt were as follows:—

I.	0·497	gave 0·1125	oxide	=22·63	per cent.
II.	0·403	... 0·0905	...	=22·45	
III.	0·470	... 0·1105	...	=23·51	
IV.	0·472	... 0·110	...	=23·30	
V.	0·5034	... 0·117	...	=23·24	
VI.	0·2399	... 0·0557	...	=23·22	
VII.	0·547	... 0·126	...	=23·03	Mean 23·05 per cent.
VIII.	0·5741	... 0·1387	...	=24·15	
IX.	0·3935	... 0·096	...	=24·39	

The last two determinations of the iron are omitted, as probably too high in calculating the mean quantity,—23·05 per cent.

I.	0·3702	gave	0·4122	carbonic acid	and	0·0705	water.
II.	0·2390	...	0·27	...	...	0·051	...
III.	0·4130	...	0·468	...	...	0·0905	...
IV.	0·4983	...	0·5665	...	...	0·113	...
V.	0·3662	...	0·4165	...	...	0·0760	...

I. 0·7052 grm. dissolved in alcohol acidulated with muriatic acid gas and precipitated with an alcoholic solution of chloride of platinum, gave 0·171 of platinum = 4·22 per cent. of ammonia, or 3·49 of nitrogen.

II. 0·4223 grm. of salt gave 0·1015 of platinum = 4·18 ammonia, or 3·45 nitrogen. Mean 3·47 per cent. nitrogen.

		I.	II.	III.	IV.	V.	
Carbon	=	30·78	31·23	31·33	31·43	31·44	per cent.
Hydrogen	=	2·11	2·37	2·43	2·51	2·30	
Oxygen	=	40·57	39·81	39·70	39·52	39·72	
Nitrogen	=	3·49	3·49	3·49	3·49	3·49	
Fe_2O_3	=	23·05	23·05	23·05	23·05	23·05	
		100·00	100·00	100·00	100·00	100·00	

The salt employed in these determinations was made at five different times. The compound is evidently a double salt, consisting of meconate of iron and meconate of ammonia. The discrepancies in the determinations are probably owing to the circumstance that one of the constituent salts is more soluble in the wash-water than the other.

Iron Salt from Ethereal Solution of Meconic Acid.

A cold ethereal solution of meconic acid was made by agitating the acid, in the state of fine powder, in a stopped bottle with anhydrous æther. A considerable quantity of æther must be employed, as the meconic acid is but very slightly soluble in that liquid. The saturated solution was then filtered into a second bottle, containing an ethereal solution of perchloride of iron. This was made by dissolving neutral perchloride of iron, which had previously been gently evaporated to dryness, in anhydrous æther. When mixed, the two liquids became of a deep red colour, and in a few minutes a quantity of reddish-brown flocks precipitated. These were collected on a filter and washed with æther till any adhering chloride of iron was removed. When dried they formed a reddish-brown powder. This can only be obtained by the use of anhydrous æther; if it contains any water, no precipitate falls, and the salt is condensed in blood-red drops on the sides of the bottle. The presence of alcohol is equally objectionable. After the salt has been dried it becomes much less soluble than before. It dissolves pretty readily in cold

water and alcohol, but more readily in hot water, and the addition of a little acid greatly increases its solubility. The colour of its solution is brownish-red. When it is treated with a slight excess of potash or soda it is instantly decolorized, and the iron precipitated in the state of peroxide. The iron of this compound is not precipitated by an excess of ammonia, and its colour is only changed to a deep yellowish-red. Dried at 212° F.,—

I.	0·3826	salt gave	0·117	peroxide	= 30·58	per cent.	
II.	0·2705	...	0·082	...	= 30·31	...	
III.	0·2307	...	0·0721	...	= 31·25	...	
IV.	0·2593	...	0·0803	...	= 30·96	...	
V.	0·3131	...	0·972	...	= 31·03	...	
					Mean 30·82	...	

I.	0·2747	salt gave	0·261	carbonic acid	and	0·0475	water.
II.	0·441	...	0·41	...	...	0·0755	...
III.	0·345	...	0·325	...	...	0·054	...

	I.	II.	III.
Carbon . . =	26·27	25·70	26·03
Hydrogen . =	1·92	1·90	1·74
Oxygen . . =	40·99	41·58	41·41
Fe_2O_3 . . =	30·82	30·82	30·82
	100·00	100·00	100·00

The salt employed in these determinations was prepared at three or four different times; but though the results agree pretty closely, I have not been able to fix upon a probable formula for the salt.

When meconic acid is agitated in the cold with freshly precipitated peroxide of iron no effect is produced, and if a slight heat is applied, only a very partial combination is effected. If the heat is increased, though much under 212° F., a large portion of the peroxide is dissolved by the acid; but if the compound is examined, much of the iron has been reduced to the state of protoxide. If the liquid is filtered, it deposits on cooling a quantity of a reddish powder, which consists of meconic acid in combination with a mixture of peroxide and protoxide of iron; sometimes the oxide amounts to as much as 34 per cent.

Komenic Acid.

This acid is easily prepared by boiling meconate of lime in a great excess of strong muriatic acid. This removes almost the whole of the base, and converts the meconic into the komenic acid. When the solution cools the impure acid is deposited in hard reddish coloured crystals. The best way of

purifying the komenic acid is to dissolve it with the assistance of heat in a slight excess of a concentrated solution of either potash or soda, and to filter the liquid while hot. This removes any portion of lime which the komenic acid may still have retained. On the cooling of the solution the komenate of potash crystallizes in white mammillated masses. These should be washed with a little cold water till the highly-coloured mother liquor is entirely removed. The salt is then easily decomposed by boiling it with an excess of pure muriatic acid, from which the komenic acid may be freed by two or three crystallizations. Komenic acid, even when pure, has usually a slight shade of reddish-yellow. This may be almost entirely removed by digesting the acid with purified animal charcoal. When heated on platinum foil it does not leave any residue.

Komenate of Ammonia.

When a slight excess of ammonia was added to a hot solution of komenic acid it immediately became of a pale yellow colour. The liquid was concentrated in vacuo over sulphuric acid. The salt crystallized partly in a confused mass and partly in short four-sided prisms. It had only a slight shade of yellow, and its powder was very white.

When dried at 212° F.:—

I. 0·9925 grm. lost 0·0945 = 9·04 per cent.
II. 1·275 ... lost 0·123 = 9·035 ...

I. 0·3832 grm. of salt burned with oxide of copper gave 0·5815 carbonic acid and 0·139 water.

II. 0·3119 grm. of salt gave 0·4723 carbonic acid and 0·1168 water.

0·4015 grm. of salt dissolved in alcohol acidulated with muriatic acid gas gave 0·22 grm. of platinum = 9·75 per cent. ammonia or 8·04 per cent. nitrogen.

	I.	II.	At.	Calculated numbers.		Per cent.
Carbon	41·96	41·86	12	Carbon	= 917·22	42·04
Hydrogen	4·03	4·25	7	Hydrogen	= 87·357	4·01
Oxygen	45·97	45·85	10	Oxygen	= 1000·000	45·83
Nitrogen	8·04	8·04	1	Nitrogen	= 177·04	8·12
	100·00	100·00			2181·617	100·00

The salt therefore is the acid komenate of ammonia with 1 atom of water of crystallization. Its formula is $\overline{K}O + NH_3 + HO + 1$ at. aq.

Komenate of Lead.

When neutral acetate of lead was added to a solution of

komenic acid it caused a whitish granular precipitate, which immediately redissolved in the excess of acid present in the liquid. This precipitate reappeared and remained permanently on the addition of more acetate of lead. The precipitate, which acquired a slightly yellow colour, was collected on a filter and washed. When dried at 212° F. it was subjected to analysis.

I. 0·5316 grm. of salt gave 0·1389 of metallic lead and 0·1295 oxide = 58·50 per cent. oxide.

II. 0·411 grm. gave 0·103 lead and 0·1295 oxide = 58·50 per cent. of oxide.

I. 0·3683 salt when burned with chromate of lead gave 0·255 carbonic acid and 0·0385 water.

		At.	Calculated numbers.		Per cent.
Carbon	= 19·14	12	Carbon .	= 917·220	19·28
Hydrogen	= 1·16	4	Hydrogen	= 49·918	1·05
Oxygen	= 21·20	10	Oxygen .	= 1000·000	21·03
PbO .	= 58·50	2	Oxide of lead	= 2789·000	58·64
	100·00			4756·138	100·00

This salt therefore is bibasic with 2 atoms water, and its formula is $C_{12}H_2O_8 + 2\,PbO + 2aq = \overline{K}O + 2\,PbO + 2aq$.

The same salt is also formed when komenate of ammonia is dropt into a solution of acetate of lead. Komenic acid appears therefore to form only one lead salt. This result is rather unexpected, as when komenic acid is neutralized with ammonia it forms a second silver salt.

The salt made from acetate of lead and komenate of ammonia was also analysed.

I. 0·5615 grm. of salt gave 0·2025 of metallic lead and 0·111 of oxide = 58·61 per cent. oxide.

II. 0·8745 grm. of salt gave 0·2075 of lead and 0·29 oxide = 58·72 per cent. oxide.

Komenate of Copper.

When a hot solution of komenic acid is added to sulphate of copper it changes its colour from blue to dark green, and after standing a few minutes, a crystalline precipitate, of the colour of Schweinfurth green, is slowly deposited. The crystals, though small, are very distinct; they are elongated pyramids of a bright green colour, but the colour of their powder is much lighter. When dried at 212° F.:—

I. 0·35 gr. of salt gave 0·117 oxide = 33·42 per cent.
II. 0·2865 ... ... 0·0955 ... = 33·33 ...
33·37 mean.

I. 0·4204 grm. of salt burned with oxide of copper gave 0·4664 carbonic acid and 0·0685 water.

II. 0·4636 grm. of salt gave 0·5225 of carbonic acid and 0·0775 water.

	I.	II.	At.	Calculated numbers.	Per cent.
C . .	30·67	31·22	12	Carbon . . . 917·22	31·00
H . .	1·81	1·85	8	Hydrogen . . 49·918	1·68
O . .	34·15	33·56	10	Oxygen . . . 1000·000	33·81
CuO .	33·37	33·37	2	Oxide of copper 991·400	33·51
	100·00	100·00		2958·538	100·00

This is evidently a bibasic salt with two atoms of water. Its formula is $\overline{K}O + 2CuO + 2\,aq$.

When komenate of ammonia is employed instead of komenic acid the same salt is also formed, but it then falls as a copious flocculent precipitate of a greenish yellow colour. 0·5507 grm. of salt gave 0·184 of oxide = 33·41 per cent.

Komenic acid also changed a solution of acetate of copper to a green colour, but produced a very scanty precipitate. The addition of ammonia did not increase the quantity of the precipitate, but gave the solution a rich blue colour.

Komenate of Silver.

Komenic acid forms two silver salts, both of which have been examined by Professor Liebig.

The monobasic salt, which is a white flocculent precipitate, is made by adding komenic acid to a solution of nitrate of silver.

I. 0·2395 grm. of salt gave 0·590 of silver = 43·64 per cent.
II. 0·4715 ... ... 0·103 ... = 43·98 ...

The calculated number is 43·93, and the formula of the salt $\overline{K}O\,AgO + aq$.

The yellow salt is formed by adding komenate of ammonia to nitrate of silver.

I. 0·313 grm. gave 0·1825 silver = 62·62 per cent. oxide.
II. 0·558 ... 0·325 ... = 62·46 ... ...

The calculated number is 62·48, with which I need scarcely add that Professor Liebig's results approach very closely.

CIII. *On the Reduction of the Salts of Peroxide of Iron by means of Vegetable Substances.* By John Stenhouse, *Ph.D.*

IN the course of some experiments I had recently occasion to observe that some of the most common vegetable substances reduce the persalts of iron with very great facility. A

quantity of common meadow grass was immersed in a tolerably dilute cold solution of persulphate of iron. In the course of half an hour, when tested with red prussiate of potash, the liquid gave a deep blue precipitate, indicating the formation of a considerable quantity of protosulphate of iron. After three days the solution was again tested, when the iron was found to have been completely reduced to the state of protoxide. Several other kinds of green vegetable matters, such as twigs of trees and shrubs, produced similar results; as did meadow-hay, chips of wood and sawdust. Peat and wood charcoal, of all the substances which I tried, appeared to be those which effected the reduction of the persulphate with the greatest rapidity. A solution was completely decomposed by either of them in less than twenty-four hours; but with the assistance of heat the reduction was effected in an hour or two. Sugar, starch, gum, spirits of wine, oil of turpentine and pieces of paper, though they produced no effect in the cold, at a boiling temperature also caused a partial reduction of the salt. The substances previously enumerated operated exactly on solutions of the perchloride of iron as on those of the persulphate.

CIV. *On the Hydrate of the Oil of Laurel Turpentine.* *By* John Stenhouse, *Ph.D.*

A FORMER communication contained a short account of a volatile oil called laurel oil of Guiana, said by Professor Christison to be obtained by incisions from a species of ocotea. It was found to consist of two isomeric oils, having the same composition, $C_5 H_4$, as oil of turpentine.

A quantity of this oil was mixed with some spirits of wine and a little nitric acid, exactly in the way recommended by M. Wiggers for procuring the hydrate of oil of turpentine. After it had stood for some months, a large portion of the oil was converted into a crystalline mass of a deep yellow colour. By dissolving it and repeatedly crystallizing it out of spirits of wine, it was readily procured in fine large rhombic prisms, which were perfectly white, and had neither taste or smell. These crystals melted at 257° F., and when heated began to sublime at about 266° F. When dried at 212° F. they were subjected to analysis in the usual way.

I. 0·2615 grm. substance gave 0·662 of carbonic acid and 0·275 water.

II. 0·3068 grm. gave 0·780 of carbonic acid and 0·321 water.

	I.	II.	Calculated numbers. At.	Per cent.
Carbon .	69·99	70·30	5 Carbon	=70·19
Hydrogen	11·68	11·62	5 Hydrogen	=11·44
Oxygen .	18·33	18·08	1 Oxygen	=18·37
	100·00	100·00		100·00

It is evident from these analyses that the crystals of hydrated laurel oil are isomeric and isomorphous with those of the hydrates of the oils of turpentine and cedar. Their most probable formula is $C_5 H_4 + HO$, or one atom oil and one atom water. This is rendered still more probable by the following experiment. When a portion of these crystals were distilled with anhydrous phosphoric acid they yielded a colourless oil, lighter than water, which had the same taste and smell as laurel oil, and appeared to be that oil regenerated. Unfortunately, from the small quantity of the crystals in my possession, I was unable to verify this by analysis.

The crystals also dissolved when gently heated in strong sulphuric acid, to which they gave a red colour. They evolved balsamic vapours which strongly reddened litmus. The addition of water precipitated the oil changed into a tenacious resin.

CV. *On East Indian Grass Oil. By* J. Stenhouse, *Ph.D.*

I AM indebted to the kindness of Professor Christison for a quantity of an East Indian grass oil, which forms the subject of the present notice. This oil is said to be the produce of *Andropogon Ivaracusa*, and is I believe what is commonly called the oil of Namur, though Dr. Royle affirms that the grass oil of Namur is derived from the Andropogon (*Calamus aromaticus*), the true spikenard of the ancients.

The oil which I have subjected to examination has a very fragrant aromatic odour, slightly resembling that of otto of roses, but not nearly so rich. Its taste is sharp and agreeable, approaching that of oil of lemons. It has a deep yellow colour, and evidently contains a good deal of resinous matter, which induces me to suspect that it is pretty old. It is lighter than water, and quite neutral to test paper.

When mixed with water and subjected to distillation, it left nearly one-half of its bulk of a fluid resin. The oil which passed into the receiver was colourless, but its smell was not quite so agreeable as before distillation, and the same was the case with the resin in the retort. The oil was rendered anhydrous by treating it with chloride of calcium and again rectifying it.

It began to boil at 297° F., but the boiling gradually rose to 320° F., when it became stationary for some time, and then continued rising. When subjected to analysis

0·3465 gr. gave 1·061 of carbonic acid and 0 3575 water.

Carbon	83·76
Hydrogen	11·46
Oxygen	4·78
	100·00

As the analysis evidently showed that the oil consisted of a carburetted hydrogen mixed with a little of an oxygenated oil, a quantity of the rectified oil was treated with small pieces of sodium. These immediately caused an evolution of hydrogen, but this ceased in a short time, and the bits of sodium which had not dissolved remained quite bright, while a small quantity of a reddish coloured resin was also formed. The oil was then poured off the sodium and rectified. When subjected to analysis

0·2675 gram. gave 0·855 of carbonic acid and 0·277 water.

		At.	Calculated numbers.
Carbon .	88·37	5 Carbon	= 88·46
Hydrogen	11·50	4 Hydrogen	= 11·54
	99·87		100·00

The grass oil consists, therefore, of a carburetted hydrogen, having the same composition, $C_5 H_4$, as the numerous other oils of which oil of turpentine is the type, together with a small quantity of one or more oxygenated oils. The affinity which this grass oil has for oxygen appears to be very considerable; for even after being purified, the carburetted hydrogen part of the oil cannot be distilled without a little of it being converted into a resin. The resinous matter, of which the oil contains such a large quantity, is, I should think, therefore most probably the effect of oxidation.

CVI. *Observations on the Pharmaceutical and Chemical Characters of the Peruvian Matico. By* John F. Hodges, *M.D.*

ABOUT five years ago I received a parcel of the leaves of the Matico from a friend who had resided many years in Peru. He informed me that they were universally regarded by the native practitioners of that country as a most valuable remedy in various diseases, and also related several marvellous stories, current among the Indians and European settlers, of their power in arresting the most violent hæmorrhages, particularly those connected with the bladder and

urinary organs. At the time I made a few experiments with the leaves, which however I was only lately able to pursue, and as they have not been subjected, so far as I can in this remote district ascertain, to a careful chemical examination either in this country or on the continent, the following observations may be interesting. It is, I believe, to Dr. Jeffreys of Liverpool that we are indebted for the first notice in this country of the medicinal virtues of the Matico. Its action, when applied externally as a styptic, has been established in the practice of Dr. Munro of Dundee, and Dr. Lane of Lancaster has also lately communicated the results of his experience regarding its internal administration, which are confirmatory of its South American reputation. On the continent, a short notice of it has appeared in the *Pharmaceutische Central Blatt*, Jan. 1843, by Dr. Martius, and a brief and imperfect account of it is also given in the *Dictionnaire* of Merat and Lenz. It is stated by Dr. Martius, that like the Gunjah, which the East Indian prepares from the *Cannabis Indica*, the leaves and flowers of the Matico have been long employed by the sensual Indians of the interior of Peru to prepare a drink which they administer to produce a state of aphrodisia.

The sample of Matico which I received consisted of the leaves of the plant, which were of various sizes, from two to eight inches long, and appeared to have been dried, as they could easily be rubbed to powder between the hands. It is indeed stated by Dr. Martius, that the Indians dry the leaves over a fire, taking care not to allow them to be touched by the flame or burnt. Another sample which I lately procured had the same appearance, but contained, mixed up with the leaves, a considerable quantity of the flowering twigs and woody stems of the plant. The leaves and twigs were compressed together and flattened into a cake.

The botanical history of the Matico appears to be but imperfectly known; and there exists a difference of opinion even as to the class of plants from which it is derived; Dr. Martius, in the *Phar. Central Blatt*, considering it to belong to the *Phlomis* tribe, while in the *Flora Peruviana* it is described as a *Piper*. By immersing a specimen of the plant, which seemed tolerably perfect, in warm water, I was able to examine it with considerable accuracy, and certainly its characters appear very unlike those which belong to the Phlomis family. The stems are woody, round and pubescent; the leaves sessile, acuminato-lanceolate, rugose and crenate, their upper surface of a dark green, and their lower of a pale green colour. It is said that the name of the plant is derived from

a Spanish soldier named Matico, who, lying desperately wounded and bleeding to death, in his agony caught accidentally some of its leaves, and by their application arrested the hæmorrhage and healed the wound. The leaves have a strong aromatic, slightly astringent taste, and the smell and taste of their infusion in water very much resembles that of the tea prepared by the country people in Ireland from the leaves of our indigenous *Salvia verbenaca*.

The following experiments were undertaken to ascertain the pharmaceutical characters of the leaves.

Experiment 1.—Reduced half an ounce of the leaves to a coarse powder and macerated in six fluid ounces of cold distilled water. In ten minutes the liquid had a pale amber colour and the specific gravity 1·003; in thirty minutes its density had increased to 1·004 and its colour had become of a deeper amber; it possessed the peculiar aromatic astringent taste of the leaves. In two hours the liquid had specific gravity 1·005, gave a deep olive precipitate with tinct. ferri muriat., and a yellow white with acetate of lead; tartrate of antimony produced no change. In three hours its colour was rather more brown, specific gravity 1·005. In five hours specific gravity 1·005½; when dropped into a solution of gelatine it produced no change. In seven hours specific gravity had not increased. In nine hours no change. The maceration having been continued for twelve hours longer, the density was not increased. The filtered liquid had a rich orange brown colour, was neutral to litmus, and possessed the smell and taste of the leaves. The following reagents were applied. Solution of gelatine, tartar-emetic, and perchloride of mercury produced no change.

Tinct. ferri muriat.	Deep black colouring and dark olive precipitate.
Acetate of lead Infusion of nutgalls	Copious canary yellow precipitates.
Sulphuric acid Nitric acid Muriatic acid	Brown-yellow precipitates.

Caustic potash deepened its colour without throwing down a precipitate. Returned the liquid to the leaves and added 6 oz. cold distilled water, which reduced its specific gravity to 1·003. In three hours its density had not increased; poured off the liquid without expression and macerated the same leaves in 6 oz. cold water. In three hours the liquid had a light yellow colour and specific gravity 1·002; gave a very minute deposit with acetate of lead. Poured off the liquid

and macerated for fourteen hours in the same quantity of water; specific gravity 1·000.

Experiment 2.—Infused half an ounce of the sub-pulverized leaves in 6 oz. boiling water. In three hours the liquid had the same taste and colour, and exhibited the same reactions as the cold infusion; specific gravity 1·006.

Experiment 3.—Exhausted $1\frac{1}{2}$ oz. of the leaves by boiling with distilled water over a water-bath and evaporating the filtered decoction to the consistence of an extract. The quantity of extract procured weighed 120 grains. It had a dark brown colour and bitter astringent taste, and possessed very little of the aromatic qualities of the leaves.

Experiment 4.—Introduced 3 oz. of the Matico leaves on a perforated metal support into a tin plate still with about two quarts of water and heated over the fire of a table furnace, adding fresh water occasionally to supply the loss. A milky liquid was given off possessing a strong aromatic camphoric odour, and tasting something like a mixture of oil of rosemary and oil of cubebs. It contained a considerable quantity of heavy oil of a light green colour, which slowly subsided to the bottom of the recipient. By returning the milky liquid to the still and distilling again with 2 oz. of fresh leaves, a liquid was procured from which about one drachm of this oil subsided.

The Oil of Matico has a light green colour; when recent it has nearly the consistence of good castor oil, but becomes thick and crystalline on keeping. Its smell is very powerful and permanent, and its strong camphoric taste remains a considerable time in the mouth. It dissolves readily in æther and in alcohol; the solutions are colourless. Sulphuric acid also dissolves it with the production of a beautiful carmine colour; water added to this solution destroys its colour and converts it into a milky liquid. Nitric acid when poured on the oil becomes of a deep amber colour, and converts it into a resinous matter. Neither caustic potash nor ammonia had any action on it. After all the oil had been separated by distillation, a deep rich red-brown liquid remained in the still; it had a bitter astringent taste, without any of the aromatic flavour of the leaves; it was neutral to litmus; the leaves were quite insipid. The filtered liquid acted towards reagents like the infusion (Exp. 1).

Experiment 5.—Added acetate of lead in excess to the filtered decoction (Exp. 4). A light olive precipitate was thrown down and separated by the filter, the excess of lead was removed by sulphuretted hydrogen from the filtered liquid, which after this treatment had a light yellow colour, and produced, with tinct. ferri muriat., merely a slight olive troubling.

Ammonia gave a canary-yellow precipitate, and fresh infusion of nutgalls a light brown precipitate. Evaporated over the water-bath, a gelatinous extract of the colour and appearance of thin glue remained. It tasted like the extract of Matico (Exp. 3), dissolved slowly in water, but was not acted on by æther or solution of potash. From its solution in water alcohol threw down a gray-coloured precipitate, acetate of lead ditto; perchloride of iron produced no change; caustic potash and ammonia rendered the solution orange, and threw down rich yellow precipitates. Neither muriatic acid, nitric acid or tartar emetic produced any change. The gelatinous extract was dissolved in distilled water, the solution was cautiously evaporated over the water-bath to the consistence of a syrup, which was placed aside in a cool place, and after some hours a number of distinct prismatic crystals had formed in it. These crystals had a brown colour and cooling taste; heated on a slip of platinum foil, they decrepitated and left a yellowish white residue, which effervesced with hydrochloric acid. In their solution in water chloride of platinum threw down a yellow precipitate. Digested the syrupy extract and crystals in alcohol of 84° (Gay-Lussac), its brown colour changed to a clear orange, and the salts collected into a gritty cake. Upon evaporating the filtered alcoholic solution, a yellowish-brown extractive matter, *maticine*, remained. It had a disagreeable smell and exceedingly bitter taste, like aloes, which remained a long time on the palate; it attracted moisture from the atmosphere, dissolved readily in alcohol and in water, but was not acted on by æther: heated on platinum foil it became brown, swelled up without decrepitation, and left a bulky charcoal. Its solution in water was not affected by chloride of platinum, but gave a yellow precipitate with solution of potash, and also with ammonia: chloride of barium did not alter its colour; tinct. ferri muriat. rendered it of a deep rich carmine colour, but did not form a precipitate.

Experiment 6.—A tincture was made by macerating half an ounce of the leaves, reduced to a coarse powder, with 4 fluid ounces of alcohol of 84°. In half an hour the liquid had a light green colour; after macerating for six days the filtered tincture had a fine brownish-green colour, and the specific gravity 0·860. It possessed in perfection the aromatic astringent taste of the leaves; water made it muddy but occasioned no precipitate; tinct. ferri muriat. gave a copious brown black, and acetate of lead a greenish yellow precipitate; solution of potash rendered its colour deep orange, and threw down a deep orange precipitate; ammonia produced a yellow precipitate.

Experiment 7.—The leaves were incinerated and gave 15

per cent. of a light gray ash, which contained the usual ash constituents. I am at the present time engaged with their quantitative examination, after the excellent method of Hertwig, *Annal d. Chemie und Pharmacie,* xlvi. Bds. 1 Heft.

Experiment 8.—When a portion of the leaves from which all the parts soluble in water had been separated was treated with æther and afterwards with alcohol, *chlorophylle* and a *dark green resin* were procured. The resinous matter was heavier than water, adhered to the fingers with great tenacity, and when heated on platinum foil burned with a strong odour of empyreumatic oil, leaving a bulky charcoal.

From the preceding experiments we may conclude that the leaves of the Matico contain the following constituents:—

1. Chlorophylle.
2. A soft dark green resin.
3. A brown colouring matter.
4. A yellow colouring matter.
5. Gum and nitrate of potash.
6. A bitter principle, maticine.
7. An aromatic volatile oil.
8. Salts.
9. Lignin.

The leaves of the Matico are easily reduced to a fine powder, which has the colour of powdered senna; when mixed with any thick vehicle, as syrup, &c., it presents an excellent mode of administering them, though, as will be evident, only adapted for extemporaneous prescription, as the essential oil, upon which it is probable much of their medicinal effect depends, would be rapidly dissipated by keeping. The cold infusion (Exp. 1), as it extracts all the active principles contained in the plant, seems the best form for obtaining its medicinal properties. The time required for its preparation need not exceed four hours, as in that time water extracts all that can be taken up by a single maceration, and but little is gained by maceration in fresh water, even though continued for a considerable time, as the liquid rapidly acquires its maximum density.

April 15, 1844.—William Thomas Brande, Esq., Vice-President, in the Chair.

Mr. Warington described a new method of covering glass, by precipitation, with a coating of metallic silver, the invention of Mr. Drayton. It consists in partially precipitating, and thus neutralizing, to use the inventor's own words, a solution of nitrate of silver by spirit of hartshorn, and adding to the clear solution, after subsidence,

oil of cassia previously dissolved in spirits of wine. This compound mixture forms the silvering menstruum, and is to be poured on to the surface of the glass, or into the vessel intended to be silvered, the surfaces having been previously rendered perfectly clean. Oil of cloves dissolved in spirit of wine is then to be gradually dropped over the surface of the silvering solution, or the two solutions may be rapidly mixed and then applied immediately. In the course of about fifteen minutes a faint purple cloud appears, and this gradually spreads through the whole of the solution, and deepens in tint until it becomes opake, when the operation is complete, and a most beautiful mirror is obtained; as thus produced the reflecting surface is darker in its aspect and more similar to the brilliancy of a very highly polished speculum. The risk of breakage attendant on the usual process, by means of tin foil and mercury, is also avoided, particularly where very large looking-glasses are being constructed, and the great advantage obtained of being enabled to silver uneven surfaces, as of lenses or cut glass. A specimen of the results of this process was exhibited.

The following paper was then read:—

CVII. *On an improved Method for the Detection and Quantitative Determination of Arsenic.* *By* Remigius Fresenius, *M.D.*

THE greater part of this paper is occupied with the discussion of the medico-legal questions arising in cases of poisoning; the author advocates the interference of the legislature to render it imperative on chemists to pursue a given method in seeking for the presence of poisons: and after pointing out the sources of uncertainty in all the methods employed hitherto for the detection of arsenic, he proposes a new one, which he alleges is free from every objection, which method is the result of many investigations pursued by himself in conjunction with Dr. von Babo.

Dr. Fresenius states the objection to the method of Reinsch to be:—1. That it does not admit of the detection of arsenic in every form in which it may exist. 2. It does not aid the detection of other poisons. 3. It contaminates the substances under examination with copper. 4. Its success in precipitating the arsenic is impeded or altogether prevented by the presence of many substances, nitrates, mercury and other metallic compounds. 5. Almost insurmountable difficulties in determining the arsenic quantitatively are attached to this method.

The method of Marsh presents these difficulties:—1. It does not admit of the separation of the arsenic under every form in which it may occur. 2. It contributes to the contamination of the substance under examination with zinc and other me-

tals. 3. The danger of mistaking antimony mirrors for arsenic. 4. Mirrors are either not formed at all, or their brilliancy is prevented, and the proof of the existence of arsenic rendered doubtful by the presence of water, of organic substances, and atmospheric air.

The method of investigating the body in cases of suspected poisoning, for the presence of arsenic, which we propose, is as follows:—

A. *Decoloration and Solution.*

The substances intended for examination are, if they consist of solid and coherent lumps, reduced into small pieces, and under all circumstances carefully intermixed. Two-thirds of the whole mixture are then put into a large porcelain basin, the remainder is kept in a well-closed vessel for unforeseen contingencies. The mixture in the porcelain basin is then drenched with an amount of fine concentrated hydrochloric acid, either equal or superior to the weight of the dry substance it contains, and with as much water as will give the consistence of a thin pap to the whole. The basin is then heated in the water-bath, and chlorate of potash in portions of about half a drachm added to the mixture at intervals of about five minutes, and until the contents of the basin has assumed a bright yellow, perfectly homogeneous and thin liquid appearance. When this point is attained, about 2 drachms more of chlorate of potash is added to the mixture, and the basin is removed from the water-bath. When completely cool, the contents are placed upon white filtering paper or upon a linen filtering cloth and the fluid allowed to run off: the residue is washed with hot water until the liquid running off no longer manifests any acid reaction: the water used in this washing operation is added to the filtrate. The whole liquid thus obtained is then concentrated in the water-bath to the weight of 1 pound (during their operation the bright yellow colour of the fluid in most cases changes into a brownish tint), and a saturated solution of sulphurous acid in water is added to the residuary, still very acid, fluid, with stirring, until the smell of the sulphurous acid becomes clearly perceptible. The whole mixture is then again heated for about an hour, until the excess of sulphurous acid is completely expelled.

B. *Separation of the Arsenic as Sulphuret of Arsenic.*

The fluid thus obtained (and which is about double the amount of the hydrochloric acid employed) is allowed to cool, and then poured into a beaker glass, and a slow stream of

washed sulphuretted hydrogen gas transmitted through it for the space of about twelve hours; the gas conducting tube is rinsed with some solution of ammonia, and the ammoniacal solution thus obtained added to the fluid in the beaker glass; this glass is then lightly covered with printing paper and kept at a very moderately warm heat (30° C.) until the smell of sulphuretted hydrogen has completely disappeared. The precipitate obtained in this manner is collected upon a filter, which ought not to be too large, and washed.

C. *Purification of Sulphuret of Arsenic so obtained.*

The precipitate obtained in B, and which besides organic matter, contains, as sulphuret of arsenic, all the arsenic originally present in the substance under investigation, and possibly moreover other metallic sulphurets, is then, together with the filter, dried in a small porcelain basin, heated in the water-bath: fuming nitric acid is added drop by drop until the whole is moistened; the moist mass is then evaporated to dryness in the water-bath. Pure, previously heated, hydrated sulphuric acid is then added to the residue, so as to moisten it uniformly; the mass is heated in a water-bath for the space of from two to three hours, and finally in the sand-bath at a somewhat higher but still moderate temperature (150° C.), until the charred mass begins to crumble. The residue is treated with from 10 to 20 parts of distilled water, until the last drops running off no longer manifest any acid reaction: the water employed in the washing is added to the filtrate.

D. *Quantitative Determination of the Sulphuret of Arsenic.*

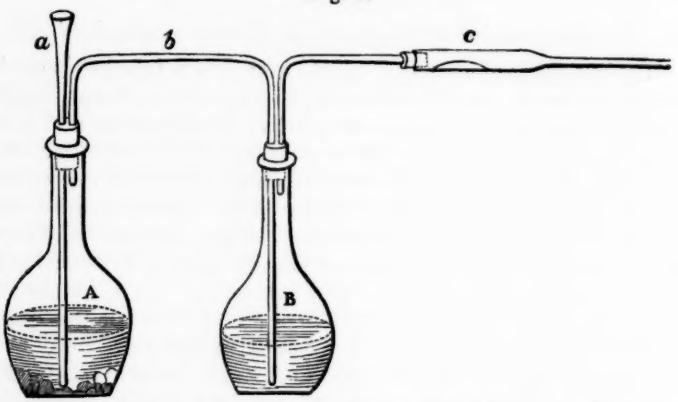
The limpid fluid obtained in C is mixed with some hydrochloric acid and precipitated by sulphuretted hydrogen, as directed in B. The precipitate, after the supernatant fluid has completely lost the smell of sulphuretted hydrogen, is filtered upon the smallest possible filter, carefully washed, and while still moist upon the filter drenched with solution of ammonia, and the filter also washed with dilute ammonia until perfectly free from the precipitate. The ammoniacal fluid is then poured into a small porcelain basin, the weight of which has previously been exactly determined, and evaporated in the water-bath; the residue is dried at 100° C. and weighed. Should the subsequent reduction prove that the residue consisted of arsenic alone, then 0·803 is the amount of arsenious acid to be reckoned for every 1000 of the sulphuret of arsenic obtained. Should a residue insoluble in ammonia have remained upon the filter, this must be tested for lead, bismuth, copper, &c. &c. Lead and mercury may moreover be present in the

charred residue of C; this latter also must therefore be further tested for the presence of these substances.

E. *Reduction of the Sulphuret of Arsenic.*

The separation of the metallic arsenic from the sulphuret of arsenic, as the key-stone of the whole investigation, requires the greatest care and attention. The apparatus sketched in fig. 1 is used for the reduction of the sulphuret of arsenic.

Fig. 1.



A is a capacious flask for the evolution of carbonic acid. It is filled to half its size with rather large pieces of solid limestone or marble (not chalk, since this last substance will not yield a continuous stream). To one aperture of the doubly-perforated cork a funnel tube *a* is adapted, which nearly reaches to the bottom of the vessel; to the other aperture a tube *b*, by means of which the gas evolved is conducted into a flask of smaller size, B; in this flask it is washed and dried by the hydrated sulphuric acid contained therein. The tube *c* conducts the carbonic acid into the reduction-tube C (which is sketched in fig. 2 of its natural size). This reduction-tube must be made of difficultly fusible glass.

When the apparatus is prepared, the little basin with the sulphuret of arsenic (vide D.) is again weighed, one-third of its contents taken off and put upon a watch-glass; the exact weight of this abstracted part is determined by substituting weights for it. The basin containing the two-thirds remaining is carefully kept. The abstracted third intended for reduction is rubbed in a small basin, previously heated in the water-bath, together with about 12 parts of a mixture consisting of 3 parts of dry carbonate of soda and 1 part of cyanide of potassium (prepared according to Liebig's method); the

completely intermixed powder is put upon a small strip of card-paper bent into the shape of a gutter. This is put into the reduction-tube up to the point *f*, and the tube is then turned half round its axis.

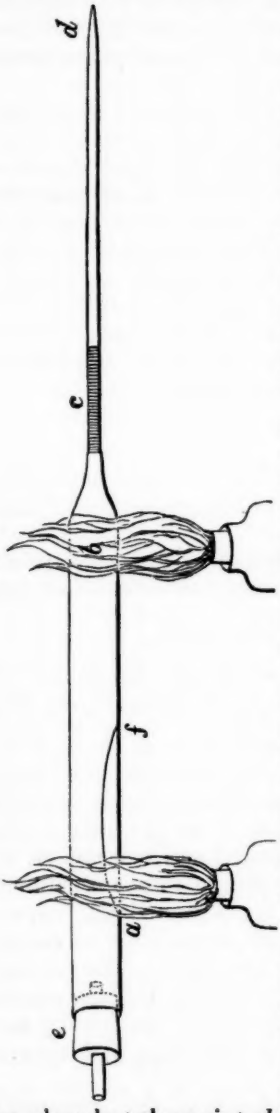


Fig. 2.

In this manner the mixture is placed at *a* of the reduction-tube without soiling any other part of the tube, the strip of card paper is then cautiously withdrawn from the tube, so as to leave the mixture undisturbed. The reduction-tube is then, by means of the cork *e*, fixed to the gas-evolution apparatus; a moderate stream of carbonic acid gas is evolved by pouring hydrochloric acid into the funnel tube (*a*, fig. 1), and the mixture most carefully dried by very moderately heating the tube along its whole length by means of a small spirit-lamp. When every trace of water has disappeared from the tube, and the gas stream has become so slow that the bubbles pass through the sulphuric acid at intervals of about a second, the spot *b* is heated to redness by means of a spirit-lamp. When this point is attained, another strong spirit flame is applied to the mixture progressing from *a* to *f*, until all arsenic is expelled (the first flame continues at the same time acting at *b*): the reduced arsenic precipitates at the spot *c* forming a mirror, whilst an exceedingly small portion escapes at *d* and fills the air with the smell of garlic. The second spirit-lamp is at last slowly advanced to the spot *b*, so as to drive towards *c* all the arsenic which has adhered to the walls of the wide tube. After this, both lamps are removed, the tube closed at the point *d* by fusion, and heat applied progressively from the point *d* towards *c*, so as to contract the

mirror on this side also, which causes it to exhibit a particularly fine and metallic appearance; the tube is then cut off at the point *f*, closed, sealed, and thus becomes a permanent evidence, which may be referred to in any future point of the legal proceedings. The remaining two-thirds of the sulphuret of arsenic (vide *supra*) are also put into a small glass tube, and this too is then closed and sealed and preserved for reference.

If sulphuret of zinc or sulphuret of antimony be present, together with the sulphuret of arsenic, the zinc and the antimony will be obtained in their metallic state upon dissolving in water the residue found in the reduction-tube (antimony is also found in the solution); they must be determined by the ordinary methods now in use. Their weight is calculated upon the whole amount of the residue originally contained in the small porcelain basin (vide D), and the weight of their corresponding sulphates subtracted from the total weight of the residue. The remainder is the amount of sulphuret of arsenic corresponding to the arsenic present.

May 6, 1844.—Thomas Graham, Esq., Vice-President, in the Chair.

Dr. Stenhouse presented a specimen of Mannite from the *Laminaria saccharina* to the Society's museum.

Andrew Paton Halliday, Esq., and John B. Anderson, Esq., were elected Members; and Mr. Robert Murray was re-elected an Associate of the Society.

The following communications were then read:—

CVIII. *On Fluorine in Recent and Fossil Bones, and the sources from whence it is derived.* *By* J. Middleton, *Esq.*

HAVING been for some time past engaged in investigations, not yet matured, on the absolute and relative quantities of fluorine in fossil bones, I was readily led to inquire into its presence, or otherwise, in recent bones. The high authority of Berzelius had indeed satisfied me on this subject, and I might not have felt a motive to examination for myself had I not lately heard the fact doubted and disputed before the Chemical Society and elsewhere with an earnestness which could only proceed from conviction. The readiness with which the authorities of the University College acceded to my request for materials, as well for this as for my more laborious investigations, left me no difficulty, and deserves my best acknowledgements.

I easily obtained conclusive evidence of the presence of fluorine in the following portions of the human skeleton, the

bones operated upon being from the dissecting-room :—The *occiput*, the *vertebræ*, the *humerus*, the *femur*, the *teeth*, the femur of a fœtus of $6\frac{1}{2}$ months.

I examined also the arm, including the scapula, of a fœtus of $3\frac{1}{2}$ months, but could obtain no evidence of the presence of fluorine in it, a result which, considering the small quantity of osseous matter involved, was, perhaps, to have been looked for.

I determined also the presence of fluorine in the entosternal bones of the sternum of a recent tortoise.

Any one who may continue to entertain doubts on this subject, and whose object is the recognition and discovery of truth, may readily convince himself by using the means employed by me. I broke a portion of the bones to be examined into small fragments, and subjected them to the action of concentrated sulphuric acid in a platinum crucible covered, as is usual in such operations, by a plate of glass endued with an etched coating of wax. I applied the flame of a spirit-lamp from time to time, so moderating the heat as to sustain action of the acid upon the materials without projection upward of the substances against the glass. I prevent the melting of the wax by keeping a muslin rag moist with alcohol upon its upper surface. The time occupied by each experiment was between five and ten minutes.

Through these and other investigations above alluded to, I have ascertained the presence of fluorine in the organic remains of Carnivora, Herbivora, Reptilia, Pisces, as also in the recent bones of men and reptiles. The increase of fluorine in fossil bones is apparently greater in proportion to the remoteness of the period at which they lived, where the character of entombment is similar. These facts, taken conjointly, seemed to me to need for their explanation a more general source of fluorine than has been heretofore I believe supposed. It occurred to me that ordinary water might be the vehicle, and if so, the presence of fluorine in recent bones would not only be accounted for, but also its accumulation in fossil bones, being filtered from the moisture circulating in the earth's crust. In order to ascertain whether facts would be found to sustain this view, I examined the following substances:—

First. A deposit, chiefly of sulphate of lime, from, as it appeared, a chloride of calcium vat, and found it to contain fluorine, though in small quantity. As it was suggested to me, however, that glass retorts used for the distillation of hydrochloric acid have been known to be thereby corroded, I did not attach much weight to the result, although I drew encouragement from it.

Second. A deposit formed in a wooden conduit pipe in a coal mine, procured for me by my friend Dr. Falconer, and found it to contain a still greater proportion of fluorine than the former.

Third. A stalactitic deposit, said to have been formed in an aqueduct in France. It was of a pure white colour, and made up of very thin and scaly concentric layers, being at the same time very incompact: it contained no fluorine.

Fourth. A stalactitic deposit from a cave in old red sandstone, furnished to me by Mr. Arrott, to whom for this and for other assistance in my investigations I am much indebted: this I found to contain fluoride of calcium to the extent of about 9 per cent. The stalactite consisted chiefly of carbonate of lime.

Fifth. The crust formed on the inside of a kettle used for the boiling of water: this I found to afford faint but distinct proof of the presence of fluorine.

Lastly. A fragment of a vein of sulphate of barytes found in the sandstone above mentioned. This also contained fluorine, though in much less proportion than the stalactite of the fourth experiment.

The above are the only substances, sufficiently diverse in their origin, which I have had an opportunity of examining, and the facts I have elicited from them seem to confirm the justness of my theory of the prime sources of fluorine in bones. It follows, as a necessary corollary, that it exists in most if not all vegetables, though perhaps in minuteness of quantity, that may enable it often to elude detection.

CIX. *On the occurrence of Mannite in the* Laminaria saccharina *and other Sea-weeds.* *By* JOHN STENHOUSE, *Ph.D.*

MORE than thirty years ago the *Laminaria saccharina*, with some others of our commonest sea-weeds, were examined by Vauquelin, who detected in several of them a sweet-tasted crystalline substance. Subsequently, in 1815, the *L. saccharina* and five other fuci were again subjected to analysis by M. Gaultier de Claubry, who also detected in the *L. saccharina* and in the *Halydris siliquosa* the same saccharine substance, which he called manna.

From the imperfect state of organic chemistry at these early periods, neither of these eminent chemists were enabled to subject this saccharine substance to analysis; and so little reliance has been placed upon their statements, that for some years past they have been generally discredited both by che-

mists and botanists; Berzelius, for instance, has not once mentioned sea-weeds as a source of mannite, though he has enumerated all the other known sources; and Dr. Greville, in his *Algæ Britannicæ*, regards the crystalline incrustations which usually appear on the *L. saccharina* and the *Halydris siliquosa* when dried, as nothing else than common salt. Under these circumstances I was lately induced to subject the *L. saccharina* and some other sea-weeds to examination.

A quantity of the dried *L. saccharina* was repeatedly digested with hot water, which formed with it a mucilaginous solution of a brownish red colour, and of a sweetish but at the same time of a very disagreeable taste. When evaporated to dryness on the water-bath, it left a considerable quantity of a saline semi-crystalline mass. This was reduced to powder and treated with boiling alcohol, by which a considerable portion of it was dissolved. The alcoholic solution on cooling became nearly solid, from the quantity of long transparent prismatic crystals with which it was filled. When purified by a second crystallization, these were deposited in large hard prisms of a fine silky lustre, and possessing all the external characters of mannite. When dried at 212° F., they were subjected to analysis.

I. 0·4334 grm. of substance gave 0·6235 of carbonic acid and 0·2995 of water.

II. 0·4215 grm. gave 0·6058 carbonic acid and 0·294 water.

	I.	II.	Calculated Numbers. At.	Per cent.
Carbon	39·78	39·74	6 Carbon	40·02
Hydrogen	7·67	7·74	7 Hydrogen	7·62
Oxygen	52·25	52·52	6 Oxygen	52·36
	100·00	100·00		100·00

It is evident from the result of these analyses, that the sweet crystalline substance in the *L. saccharina* is nothing else than mannite. The quantity of mannite contained in it is very considerable. One thousand grains of the dried sea-weed, when treated in the way already described, first with water and then with alcohol, gave 121·5 grains = 12·15 per cent. The specimen operated on had been kept for six months, and was covered with an incrustation in long slender needles. I also examined a quantity of the fresh sea-weed, and found it to contain as much mannite as the older specimen. It appears, therefore, that the epithet *saccharina*, as applied to this species of Laminaria, is not so inappropriate as has been often supposed.

Mannite may be easily distinguished from cane-sugar by the following test. If a little strong sulphuric acid is poured

upon the mannite and a gentle heat is applied, the mannite dissolves without being in the least discoloured, and gives a transparent solution. If the heat is much increased the liquid becomes of a deep brown colour, but does not lose its transparency. When cane-sugar, on the contrary, is gently heated with sulphuric acid, it is, as is well known, immediately charred with evolution of sulphurous acid gas. From grape-sugar mannite may be likewise easily distinguished. If mannite is boiled with a strong solution of potash or soda, it dissolves without any change of colour, while grape-sugar when similarly treated acquires a deep brown colour. When heated with a solution of potash and some sulphate of copper, mannite completely prevents the precipitation of the oxide of copper, while grape-sugar causes the immediate precipitation of the red oxide of copper.

Besides mannite, the *L. saccharina*, in common with most of the other sea-weeds, contains a great deal of a peculiar mucilage, which when dried has a deep reddish colour. It differs however from ordinary gum, for when digested with nitric acid it yields oxalic, but neither mucic or saccharic acids. I intend subjecting this substance to more minute examination.

L. digitata.—Besides the *L. saccharina* I have also examined some of the other sea-weeds for mannite, and among others the *L. digitata* or common tangle. The aqueous solution of this sea-weed is also reddish brown, and when evaporated it yields a similar mucilage with the *L. saccharina*, but in much smaller quantity. The *L. digitata* also contains a considerable quantity of mannite, though I should think scarcely half as much as what exists in the *L. saccharina.*

Halydris siliquosa.—The next sea-weed examined was the *Halydris siliquosa.* With hot water it forms a very dark-coloured solution of a bitter and slightly astringent taste. The quantity of mannite contained in it is very great, amounting I should think to between 5 and 6 per cent. As already mentioned, mannite forms a great part of the white incrustations which appear on the surface of this sea-weed when dried.

Alaria esculenta.—This beautiful sea-weed, which is by no means uncommon on the coasts of Scotland, where, as its name imports, it often serves as an article of food, also contains mannite in considerable abundance.

Rhodomenia palmata.—*Rhodomenia palmata*, or common dulse, contains a good deal of a sweet-tasted greenish-coloured mucilage. It also yields a considerable quantity of mannite, amounting probably to 2 or 3 per cent.

Fucus vesiculosus.—The *Fucus vesiculosus*, the most common perhaps of British Algæ, contains I should think from 1 to 2

per cent. of mannite, and the *Fucus nodosus*, also a very common sea-weed, likewise yields a small but very appreciable quantity of the same principle.

Fucus serratus.—This sea-weed also contains a considerable quantity of mannite, less perhaps than the *L. digitata*, but more than the *Rhodomenia palmata*. The mannite which the *Fucus serratus* yields is much freer from colouring matter than that from any of the other Algæ, being nearly colourless from the first.

I could not detect any mannite in the *Ulva latissima* or Laver. The experiment was made on a very small scale, and will be repeated on the first opportunity. The Laver contains a good deal of a sweet-tasted green-coloured mucilage, similar to that of the *Rhodomenia palmata*.

As mannite has occurred in eight out of nine of the sea-weeds which I have happened to examine, it probably exists in larger or smaller quantity in most sea-weeds, in which it appears to replace the cane- and grape-sugar so abundant in many of our land-plants. It is evident also that mannite occurs much more plentifully in nature than has been hitherto imagined. The following is a list of the Algæ just described, arranged in order according to the quantity of mannite which they severally contain :—

1. Laminaria saccharina.
2. Halydris siliquosa.
3. Laminaria digitata.
4. Fucus serratus.
5. Alaria esculenta.
6. Rhodomenia palmata.
7. Fucus vesiculosus.
8. Fucus nodosus.

The quantity of mannite in the *L. saccharina* is such that I think mannite might be more œconomically procured from this sea-weed than from the usual source, manna.

Supposed existence of Mannite in the Roots of Triticum repens, *or Couch-grass.*

In a note on the article Mannite, in the eighth volume of the last German edition of Berzelius's *Lehrbuch*, it is stated that Professor Pfaff had succeeded in obtaining mannite from the roots of *Triticum repens*, or couch-grass. M. Pfaff says that he treated the extract of the couch-grass roots with boiling alcohol, which on cooling deposited a number of long needle-shaped crystals, which he believed to be a new species of sugar, but which Berzelius is rather disposed to regard as more probably mannite. I have twice repeated M. Pfaff's experiment on two different quantities of couch-grass roots, but with very opposite results. The alcoholic solution on standing deposited it is true a quantity of long slender cry-

stalline needles. These, however, had not a sweet taste, and when thrown into hot sulphuric acid they dissolved with effervescence without blackening the solution. When heated on platinum foil they melted, and left a white fusible alkaline residue, which, when neutralized with muriatic acid, produced a yellow crystalline precipitate in an alcoholic solution of platinum. I have every reason to believe, therefore, that these acicular crystals were merely binoxalate of potash. The grass roots certainly contained a great deal of an uncrystallizable sugar which readily fermented.

CX. *On the Composition of some varieties of South American Guano; with the description of a new mode of estimating Ammonia, and of a process for separating Lime from Magnesia, when these earths exist in combination with Phosphoric Acid.* *By* J. Denham Smith, *Esq.*

THE results of the following examinations of guano, necessary as a matter of business to myself, may prove of some interest to the Society, as they serve to confirm, in most points, those arrived at by previous analysts, especially with respect to the variableness of the composition of this substance. When I commenced these analyses I had but one sample of guano in my possession, which came through the hands of a broker in 1842, of the purity of which I could not be certain before analysis. Subsequently I was successful in obtaining genuine samples of South American guano direct from the warehouses of the importers, the bulks from which these specimens were taken being at the present time in the course of consumption in this country.

South American guano, as imported, presents itself in three distinct states, although these varieties are often mixed together in the same bag. The larger proportion of it consists of a damp pulverulent substance of various tints of brown, intermixed with nodules, usually of a lighter colour than the powder; some of these nodules are soft, easily crushed by the finger, and often present light brown silky crystals when broken; others are much harder, of a dirty white and uniform texture throughout.

The second variety exists as large concretions, often weighing several pounds, presenting various aspects when broken; sometimes appearing merely to be the first variety in a coherent, instead of a pulverulent state; at other times as a regularly stratified deposit of different shades.

The third description of guano occurs in irregularly shaped masses, very heavy in comparison with the other varieties, and termed "stones" by the labourers; when broken, this variety presents a crystalline fracture, resembling a fused salt of a brown colour; it appears to exist in large quantities in the guano when imported, for at the warehouses whence I obtained my samples, I was told that at least a hundred tons of it had been picked from the guano they had hitherto sent out for consumption. For the sake of distinguishing this variety, I shall term it "Saline Guano," whilst the second kind I shall call "Concrete Guano."

After a preliminary qualitative examination of these varieties of this manure, the utility of another and probably more exact mode of estimating ammonia than by condensing the gas in hydrochloric acid and evaporating the solution to dryness, and a more œconomical and less troublesome plan than by a salt of platina, became obvious. I therefore had recourse to an indirect method of analysis, that of estimating the ammonia from the quantity of carbonate of barytes obtained. I preferred a salt of barytes to any other substance forming a true neutral carbonate, on account of the high atomic number of barium, and its consequent capability of expressing with exactness the quantity of ammonia, as well as the great delicacy of a salt of barytes in evidencing the existence of carbonate of ammonia, for which purpose this substance is superior to a salt of lime, or even to lime water.

The point which appeared most likely to occasion error was, that the carbonate of ammonia might not be obtained as a true neutral carbonate; as a basic carbonate would of course vitiate the results, and the frequency of the occurrence of such combinations we all know since the publication of Rose's excellent paper on this subject. Experiment showed that the neutral carbonates of potash and soda, distilled with a solution of an ammoniacal salt, afforded a basic carbonate of ammonia, the solution being alkaline after a salt of barytes had been added until no further precipitate fell, and that a current of carbonic acid gas produced a precipitate in such a solution when filtered. The acid carbonates of soda and potash answered well enough where the ammonia existed in small quantities, but when a large proportion of the volatile alkali was present in the liquor subjected to distillation, the distilled solution evidently contained a basic carbonate, as when the ordinary carbonates of soda and potash were used. It now remained to be proved whether the acid carbonates of ammonia would afford correct results. To determine this point, 59 grs. of sesquicarbonate of ammonia, taken from the centre of a lump,

were dissolved in cold water and precipitated by excess of nitrate of barytes, the solution being exposed to the air in an open dish for twenty-four hours: this precipitate, collected, washed and dried, weighed 98·07 grs., indicating an excess of ·012 in estimating ammonia, merely an error of experiment to this trifling amount. The solution when gently heated evolved a little carbonic acid, but did not deposit any carbonate of barytes. Satisfied by this experiment that the acid, as well as the neutral carbonates of ammonia, precipitate a barytic salt equiatomically as respects the bases, and therefore that the proposed plan of indirect estimation of ammonia was an accurate one, I subjected 54 grs. of muriate of ammonia to distillation with an excess of a solution of the ordinary carbonate of soda, carrying on the distillation until about one-half of the liquid had passed into the receiver, in which distilled water was of course placed; long before this quantity of liquid was distilled a slip of turmeric paper suspended from the tubulure of the retort ceased to be reddened; the contents of the receiver, a solution of a basic carbonate of ammonia, were added to a solution of nitrate of barytes, and then subjected to a stream of carbonic acid gas until the precipitate became arenaceous and the solution slightly affected litmus paper; this exposed to the air for a day, and the precipitate collected, and dried, gave 97·63 grs. of carbonate of barytes. As in the former case, the filtered solution when gently heated gave off a little carbonic acid gas, but deposited nothing. These results being so favourable, and the process simple, the trifling deficiency evidently being traceable to defective manipulation alone, I have adopted this process for estimating ammonia in the analyses subsequently detailed, considering it susceptible of greater accuracy than the hydrochloric acid method, and as accurate as, and far less troublesome and expensive than, the employment of salts of platinum, and of alcohol for this purpose.

The process for separating the phosphate of lime from the phosphate of magnesia depends upon the insolubility of the oxalate of lime in very dilute acetic acid, and the solubility of the magnesian salt in that menstruum. Thus, when a solution of these mixed phosphates in hydrochloric acid is treated with ammonia slightly in excess to precipitate the characteristic gelatinous precipitate, and acetic acid is gradually added till such precipitate is redissolved, the solution being acid to litmus paper, but only faintly so to the taste, oxalate of ammonia produces the characteristic precipitate of oxalate of lime, which base is completely thrown down; the filtered solution, when evaporated and treated with a little phosphate of soda and ammonia, affording the ammoniacal magnesian

phosphate, which contains no lime. I do not give this process as one which is necessarily rigidly accurate, for if the acetic acid be in too great excess, more than completely sufficient to redissolve the precipitate produced by ammonia, the clear solution, although containing no magnesia, will at times, as I have found, give indications of the existence of lime on supersaturation with ammonia; but the quantity under such circumstances held in solution is too small to be of importance except in cases where a scientific point is involved. Where oxalate of lime is in solution together with the magnesian and calcareous phosphates, this process requires some modification, which it may be better to explain in the details of the mode I have adopted in the analysis of guano, than at present—that recapitulation may be as much as is possible avoided.

It may be advantageous here to describe the mode of analysis pursued in the examination of these samples of guano, as each analysis, in fact, consists of three separate ones, viz. of those portions soluble in cold water; the substances which dissolved on boiling the residue insoluble in cold water, in abundance of water; and the portion which remained insoluble in either menstruum. This division I found to be a very convenient one, as the solutions obtained were far less complex than if the portions of the guano soluble in water cold and hot, and in acids, had been mixed together; and it of course gives a pretty correct idea of the salts as they actually are presented to the roots of plants manured with guano. My reasons for combining the bases and acids as I have done in the results of these analyses are, that in some cases the proportional quantities of acid and base have tallied, and also that I have obtained by crystallizing the hot and cold solutions, oxalate of ammonia, oxalate of soda, muriate of ammonia, chlorides of potassium and of sodium, sulphates of soda and potash, urate of ammonia and free uric acid, from the various samples of guano; and also that by microscopic examination crystals of the chlorides and of sulphate of soda have been readily observed in the mass of the guano. As I have also given the amount of bases and acids obtained without reference to the state of combination in which they exist, those who differ from me in this respect, can combine them as they think proper.

The mode adopted for determining the respective amounts of the fixed alkaline bases is open to many objections. It is complex; a very slight error in weighing is liable to considerably vitiate the result: if the whole numbers I have adopted as representing the combining equivalents of the va-

rious acids and bases are incorrect, so also must the results be. On the other hand, I have tried this method upon an actual mixture of soda and potash salts, and the results approximated very closely to the truth; and upon the whole, weighing the advantages of this indirect system of Griffin's with the positive modes of estimating the potash, either by perchloric acid, tartaric acid or platina salt, I believe this indirect mode to afford, in careful hands, at least as accurate returns, if not more so, than the direct modes of estimating the potash, and ascertaining the soda from the loss. I may be wrong in attributing this process to Mr. Griffin, as Barreswil and Sobrero assign it to M. Mayer, with a date anterior to Griffin's description in the Philosophical Magazine.

With respect to the neutral phosphate of lime stated to exist in the sample of "Concrete Guano, No. 6," and also in No. 2, I may state that it precipitated as neutral phosphate; and if I had estimated it as bone-phosphate, the sum of the analysis would have fallen very far short of the quantity employed; whilst by estimating it as I have done, the loss was most trivial, amounting only to a common error of analysis. Of the solubility of the phosphate of lime, and of the ammoniacal magnesian phosphate in boiling water, it is simply necessary to refer to the already established solubility of these salts in neutral solutions containing organic animal matter, and also to state that these solutions were invariably faintly acid to litmus paper.

I was led to suspect the existence of a volatile acid in guano, but I in vain tried to isolate it, if indeed it exists, and the acid odour and reaction are not truly to be attributed to the reaction of the sulphuric or phosphoric acids, the agents made use of in the attempt, upon the organic portions of the guano.

The quantity submitted to analysis was in each case either 300 or 500 grs., and the results were calculated to 1000 parts for the convenience of ascertaining the per-centage, and for greater readiness of comparison.

The water was determined approximately, by drying till the portion lost no more weight, without any sublimation taking place. Water and ammonia were volatilized. This estimation of the water was corrected by subtracting the sum of the weight of the soluble salts, and portions insoluble in cold water, ascertained during the subsequent process, from the original weight of guano employed. A given weight of the sample of guano to be examined was ground up with cold distilled water; when the insoluble portions had subsided, the solution was passed through a filter and the residue washed with two or three successive portions of distilled water; the

insoluble residue was then placed on the filter, and treated with distilled water until salts of lime and barytes, being added to a few drops of the solution, gave no precipitate, or but a faint trace of one. The insoluble residue was dried at 212°, its weight was noted, and the aqueous solution, which usually amounted to about a pint and a half, was accurately measured, and its quantity made up to exactly 32 or 40 fluid ozs. This solution, when freshly prepared, was generally neutral or slightly acid; in no one instance have I found it alkaline, but it became so when kept in a stopped bottle for some days.

One-sixth or one-eighth of this solution acidified with nitric acid and treated with nitrate of silver gave the amount of chlorine—hydrochloric acid. The same quantity similarly treated, but with barytes instead of silver, indicated the quantity of sulphuric acid.

Another portion, slightly acidified with acetic acid (a few drops are sufficient), and treated with hydrochlorate of lime, gave, if any oxalic acid were present, the amount of that acid, the precipitate of course being treated in the usual way; to this filtered solution, having previously boiled it and taken care that an excess of lime salt was present, was added excess of ammonia, which precipitated the phosphoric acid as bone-phosphate; this result was corrected by the weight of phosphate of silver obtained during a subsequent operation.

The quantity of ammonia was determined by distilling one-fourth or one-sixth of the solution in the mode described in a foregoing part of this paper.

If potash and soda were both found to exist in the solution by previous experiment, the following operation was carried completely out; if one only of these alkalies were present, the process was discontinued when the weight of the alkaline sulphate had been determined. One-fourth at least of the solution was gently evaporated, by which it became markedly acid; this evaporation was carried to dryness till no more water was given off, taking care to avoid volatilization of any salt of ammonia, although uncombined ammonia had been liberated during the evaporation; when quite dry it was confined for a few hours over a mixture of powdered lime and sal-ammoniac, then the vessel containing the residue of the evaporated solution was gently warmed and weighed; this afforded the quantity of solid matter contained in the cold aqueous solution, together with traces of water combined with salts and organic matter. This residue was then ignited, the organic matter and ammoniacal salts were expelled, and the loss, deducting from it the weight of the salts of ammonia, was estimated as organic matter with a little water; the fused residue was dissolved in

water and precipitated by nitrate of silver; this precipitate, when collected, fused and weighed, and the fused salt of silver treated with nitric acid and its loss of weight noted, expressed the quantities of phosphoric acid and chlorine contained in the fused saline residue. To the original solution hydrochloric acid in slight excess was added; the chloride of silver thus formed was separated, and the clear solution was evaporated with so much diluted sulphuric acid, as would have been sufficient to convert the whole of the fused saline residue into sulphate of soda, had it consisted entirely of chloride of sodium; this evaporation being very carefully conducted and the residue transferred to a platinum crucible, in which it was heated to full redness until no more acid fumes were given off, the crucible with its contents was accurately weighed, and the weight noted; if one alkali only was present, its weight was calculated from that of the sulphate; but if both potash and soda were contained in the specimen of guano under examination, the mixed sulphates thus obtained were dissolved in water, the solution was treated with a salt of barytes in the usual way, and the resulting sulphate of barytes was weighed with the most scrupulous care. The respective weight of each alkaline sulphate contained in the solution was then calculated by the following formula, which I subjoin, as the steps in the calculation are much more readily perceived in figures than expressed in words:—

$KOSO_3\ BaOSO_3\ KOSO_3\ BaOSO_3\ NaOSO_3\ BaOSO_3\ NaOSO_3\ BaOSO_3$

88 : 116 : : 1 : 1·31818 . 72 : 116 : : 1 : 1·61111

$-1{\cdot}31818 = 0{\cdot}29293$ the difference. Let the weight of the mixed sulphate be 48·54 grs., then $1{\cdot}31818 \times 48{\cdot}54 = 63{\cdot}984 - 70{\cdot}525$, weight of sulphate of barytes obtained by experiment $= 6{\cdot}541 \div 0{\cdot}29293 = 22{\cdot}33$ sulphate of soda $- 48{\cdot}54 = 26{\cdot}21$ sulphate of potash, and from these weights the respective proportions of the bases may be calculated*.

The actual amount of the chlorine or hydrochloric acid, the sulphuric, phosphoric and oxalic acid, of the ammonia, potash, soda, organic matter, &c., contained in the cold aqueous solution, were ascertained by calculation, as well as that of the water.

The residue insoluble in cold water was then ground to powder, and a known weight of it was boiled with three or four successive half-pints of distilled water, for about an hour after each addition of water; the mixture was then allowed to deposit the undissolved portions, the solution being kept hot during this subsidence and filtered whilst still at that temperature.

* See Phil. Mag. vol. xiii. pp. 132 *et seq.* and Barreswil and Sobrero's *Appendice aux Traités d'Analyse Chimique*, p. 41.

When water boiled upon this residue came off colourless, and contained only minute traces of soluble matter, the insoluble portion was collected on a filter, dried at 212° and its weight noted. The mixed solutions being gently evaporated to dryness, the product was weighed and treated with cold water, the weight of the matter insoluble in the cold water was noted, and the substance reserved; the solution obtained by thus treating it, being again evaporated to dryness, was weighed, ignited, and the loss of weight noted, indicating the organic matter, with traces of water and ammonia; the fused residue was treated with water, the filtered solution precipitated with nitrate of silver, and the weight of the phosphate of silver was ascertained; this was assumed to be due to the presence of phosphate of soda, but the quantity was always too small to ascertain whether this alkali or potash was present; the portion insoluble in water was then dissolved in a little hydrochloric acid and treated in the manner before described, to estimate the proportion of phosphate of lime and phosphate of magnesia.

The reserved portion, which was insoluble in the cold water, was then treated to ascertain the existence and proportion of free uric acid. It was boiled in successive small portions of water, four or five fluid ounces each time, until the solution ceased to become turbid on cooling; these solutions were mixed together, boiled, and allowed to cool very gradually: if free uric acid were present a few crystalline grains of this substance would be deposited, which, when weighed, were ascertained to be uric acid by means of potash and nitric acid. The portion left undissolved by these small portions of boiling water was then treated with a few drops of very dilute potash, the absence of ammonia was proved by test-paper, and the solution precipitated by sulphuric acid, which threw down the uric acid as a voluminous precipitate, which by repose was converted into crystalline grains; this was weighed, added to the weight of uric acid previously obtained, and the loss was estimated as organic matter: the solution of urate of ammonia was evaporated, its weight ascertained, then ignited, and the ashes, if necessary, analysed for lime and magnesia, in the manner before described.

The third division of the analysis was commenced by ascertaining, by means of potash, whether any uric acid or urate of ammonia was present in the residue left undissolved by the repeated boiling with water. If these substances were absent, care being taken at the same time to note whether the residue gave off any ammonia when thus treated, and the presence or absence of ammonio-phosphate of magnesia being thus ascertained, (supposing no urate of ammonia nor uric acid existed in

the residue) a given weight of it was boiled with diluted muriatic acid and filtered; in no one instance did any evolution of carbonic acid take place; the solution was then treated with ammonia in excess, which precipitated the oxalate and subphosphate of lime, perhaps the magnesia also; acetic acid was then rapidly added until it was distinctly acid to litmus paper, and a slight acidity could be detected by the taste; the insoluble precipitate being collected, thoroughly washed, dried, and ignited with the usual precaution, indicated the amount of the oxalate of lime; this precipitate was invariably examined for phosphate of lime; if it contained any, this was separated in the state of bone-phosphate and estimated as neutral phosphate, in which state of combination it existed mixed with the oxalate of lime.

To the acetic acid solution excess of oxalate of ammonia was added, this precipitated the lime present in the solution originally as bone-phosphate, sometimes mixed with neutral phosphate of lime, and from the weight of the resulting carbonate of lime, and the loss of weight sustained by ignition of another portion, correcting each other, the amount of the phosphate of lime was calculated. The filtered solution evaporated until a slight pellicle began to form, was treated with ammonia in excess, and a little phosphate of soda, observing the usual precautions recommended by Berzelius, and the resulting ammoniacal phosphate of magnesia was collected and weighed. The portion insoluble in hydrochloric acid being treated with potash gave a solution possessing the properties described to belong to an alkaline solution of the substance termed humus or humic acid; this was precipitated, collected and weighed; the residue insoluble in potash was weighed and ignited, the loss of weight noted, and the product treated with hydrochloric acid; if effervescence ensued on this addition from the presence of carbonate of lime, this was estimated as oxalate, and was added to the amount already obtained of that salt; by these means the proportion of the organic matter insoluble in potash, the humus, oxalate of lime (if any), sand, &c. &c. undissolved by hydrochloric acid, were obtained.

The proportions in which these substances existed in the guano were then ascertained by the necessary series of calculation.

Where the proportions of acid and base, as ascertained by analysis, did not exactly agree, the estimate derived from the quantity of the acid was preferred, as being far less subject to error than the process for estimating the respective amounts of the potash and soda; the requisite loss or gain was always placed to the soda, and this will account for the differences of

the losses sustained between the constituents of these samples of guano when combined, and the table, which shows the constituents according to the results of analysis.

I cannot deny that this mode of analysis is extremely tedious and complex, and I fear that this complexity, combined with a wish to avoid all unnecessary prolixity of description, has rendered its details in many places obscure. I could wish to have described a simpler and shorter mode; but in a product consisting of some fifteen to twenty substances in various states of combination, a simple mode and brevity of description of analysis are I fear impossible. For ordinary purposes of estimating the comparative value of a sample of guano, this mode of analysis is both unfitted and unnecessary, the estimation of the amount of uric acid, of ammonia, of phosphate of lime and magnesia, with the sand, &c., being quite sufficient for such purposes, and a more detailed analysis would, in the majority of cases, be both time and trouble thrown away.

Composition of a sample of South American Guano in my possession since 1842.—This guano was of the colour of Lundyfoot snuff, with dirty white lumps intermixed, varying in size from that of small shot to that of marbles. The quantity submitted to analysis was 500 grs.

No. 1.

	Calculated Composition.		*Constituents.*	
Soluble in cold water.	Moisture with combined water	222·00	Moisture and combined water	222·00
	Muriate of ammonia	25·5	Hydrochloric acid	17·50
	Sulphate of potash, trace of sulph. soda	80·0	Sulphuric acid	36·40
	Oxalate of ammonia	74·0	Oxalic acid	50·30
	Phosphate of ammonia	63·3	Phosphoric acid	43·00
	Organic matter	15·0	Potash	43·71
			Ammonia	52·05
			Organic matter	15·00
Soluble in boiling water.	Urate of ammonia	154·18	Uric acid	165·23
	Uric acid	25·16	Ammonia	14·77
	Animal matter, with water and trace of ammonia	11·80	Phosphoric acid	4·19
	Phosphate of magnesia and ammonia	5·64	Lime	1·00
	Phosphate of soda?	1·20	Magnesia	0·77
	Phosphate of lime	1·86	Soda?	0·57
			Animal matter, water	13·31
Insoluble in water.	Oxalate of lime	25·60	Oxalic acid	14·40
	Phosphate of lime	197·50	Phosphoric acid	102·03
	Phosphate of magnesia	20·30	Lime	118·72
	Sand, &c.	15·60	Magnesia	7·25
	Humus	26·36	Sand, &c.	15·60
	Other organic matter with combined water	34·56	Humus	26·36
			Water, with organic matter	34·56
	Loss	0.44	Loss	1·28
		1000·00		1000·00

The next sample very much resembled the guano just described, in its physical character; some of the small lumps were of a dirty white colour, and when broken showed no appearance of crystalline structure; these were chiefly composed of phosphate of lime; others showed brown silky crystals in the interior, which, examined under the microscope, appeared to be sulphate of soda and oxalate of ammonia. This, as well as all the succeeding varieties of guano mentioned, was obtained in January last; this specimen was considered by the importers to be of a very superior quality. The quantity analysed was 500 grs.

No. 2.

		Calculated Composition.		*Constituents.*
Soluble in cold water.		Water	215·10	215·10
		Organic matter with combined water	61·74	61·74
		Sulphate of soda	37·90	
		Phosphate of soda	35·82	
		Phosphate of lime	12·56	
		Phosphate of ammonia with some biphosphate	30·06	
		Phosphate of potash	20·02	
		Muriate of ammonia	35·22	
		Oxalate of ammonia	100·38	
		Sulphuric acid		21·06
		Phosphoric acid		55·02
		Oxalic acid		68·18
		Hydrochloric acid		24·14
		Lime		6·56
		Ammonia		51·68
		Potash		11·44
		Soda		33·70
Soluble in boiling water.		Urate of ammonia	25·12	
		Phosphate of ammonia and magnesia	4·04	
		Phosphate of soda?	1·28	
		Phosphate of lime	2·88	
		Animal matter	6·38	
		Phosphoric acid		4·30
		Magnesia		0·56
		Ammonia		2·66
		Soda?		0·60
		Uric acid		23·08
		Lime		1·26
		Animal matter and water		7·40
Insoluble in water.		Oxalate of lime	107·26	
		Phosphate of lime	192·00	
		Phosphate of magnesia, trace of ammonio-phosphate	19·84	
		Humus	20·60	20·60
		Organic matter	11·40	11·40
		Water	42·42	42·42
		Sand, &c.	16·48	16·48
		Oxalic acid		60·32
		Phosphoric acid		103·96
		Lime		145·74
		Magnesia		7·08
		Loss	1·50	3·52
			1000·00	1000·00

Two other samples of a similar character, but much darker in colour, were qualitatively examined: one, No. 3, contained substances similar to No. 2, both soda and potash, some urate of ammonia and very little sand and dirt; the other, No. 4, was almost destitute of urate of ammonia or uric acid, the faintest trace being discoverable by nitric acid and ammonia, but in too small a proportion to enable me to isolate a particle

of the acid even when acting on 3 to 500 grs. This guano also contained 17 per cent. of sand, &c., consisting apparently of sea-sand mixed with little lumps of granite, and a very dense black sand, resembling Iserine or Menachanite.

The first lump of the "Concrete Guano," No. 5, was about the size of a human skull, soft enough to be readily shred with a knife, and uniform throughout, presenting the appearance of a dark brown mass containing a vast number of minute dirty white granulations. Its scent was very slight, and neither this nor any of the other samples had an ammoniacal odour, but merely the peculiar smell possessed by South American guano. When shred and thoroughly mixed the powder was damp, and almost as dark-coloured as Nos. 3 and 4; very different in this respect from the samples 1 and 2, the analyses of which have already been detailed; 500 grs. was the quantity analysed.

Concrete Guano. No. 5.

	Calculated Composition.	
Soluble in cold water.	Water	204·2
	Oxalate of ammonia	93·9
	Phosphate of ammonia	61·24
	Phosphate of potash	77·32
	Sulphate of soda	259·44
	Chloride of sodium	29·22
	Organic matter	6·68
Sol. in boil. wat.	Phosphate of magnes. and ammonia, and trace of phosp. soda	7·84
	Organic matter	8·60
Insoluble in water.	Oxalate of lime	109·58
	Phosphate of lime	62·70
	Phosphate of magnesia	8·74
	Humus	8·62
	Sand, &c.	7·20
	Water	49·74
	Loss, &c.	4·98
		1000·00

	Constituents.	
Soluble in cold water.	Water	204·2
	Oxalic acid	63·78
	Phosphoric acid	79·50
	Sulphuric acid	144·14
	Ammonia	50·00
	Potash	38·42
	Sodium	11·09
	Soda	115·30
	Chlorine	18·13
	Organic matter	6·68
Soluble in boil. water.	Magnesia	1·08
	Ammonia	0·81
	Phosphoric acid	3·89
	Water and animal matter	10·66
Insoluble in water.	Lime	81·78
	Oxalic acid	61·64
	Magnesia	3·12
	Phosphoric acid	34·48
	Sand, &c.	7·20
	Water	49·74
	Humus	8·62
	Loss	5·74
		1000·00

The second sample of "Concrete Guano," No. 6, was much harder than the former, and appeared to have been deposited in strata; the colour was lighter than any of the preceding samples and the powder drier; 300 grs. were analysed.

No. 6.

	Calculated Composition.	
Soluble in cold water.	Water	106·66
	Muriate of ammonia	4·43
	Chloride of sodium	9·50
	Phosphate of potash	14·94
	Sulphate of soda	12·23
	Organic matter	2·40
	Oxalate of ammonia	a trace
Sol. in boil. wat.	Organic matter	10·00
	Phosphate of lime, trace of magnesia	11·37
	Phosphate of soda	a trace
Insoluble in water.	Sand, &c.	20·43
	Humus, organic matter, &c.	29·73
	Phosphate of lime	664·47
	Phosphate of magnesia	30·56
	Water	80·60
	Loss	2·68
		1000·00

	Constituents.	
Soluble in cold water.	Water	106·66
	Chlorine	8·66
	Phosphoric acid	6·40
	Sulphuric acid	6·80
	Organic matter	2·40
	Ammonia	1·40
	Potash and soda not separated	19·07
Sol. in bo. wa.	Organic matter	10·00
	Phosphoric acid	5·25
	Lime	6·12
Insoluble in water.	Organic matter, humus, &c.	29·73
	Sand, &c.	20·43
	Phosphoric acid	385·60
	Lime	298·53
	Magnesia	10·90
	Water	80·60
	Loss	1·45
		1000·00

Having previously described the characteristics of "Saline Guano," No. 7, it is needless to recapitulate them here: it is deliquescent, and the solution yielded crystals of oxalate and sulphate of soda, and the chloride of that base. 300 grs. afforded on analysis—

Saline Guano. No. 7.

	Calculated Composition.	
Soluble in cold water.	Water	77·00
	Sulphate of soda	191·77
	Oxalate of soda	105·63
	Phosphate of soda	3·60
	Phosphate of potash	49·47
	Chloride of potassium	41·63
	Chloride of sodium	286·31
	Muriate of ammonia	30·30
	Organic matter with combined water	25·53
Soluble in boil. water.	Phosphate of lime	1·10
	Phosphate of ammonia and magnesia	1·33
	Animal matter and water	7·56
Insoluble in water.	Sand, &c.	4·20
	Oxide of iron and alumina	1·50
	Phosphate of magnesia	25·80
	Phosphate of lime	131·13
	Humus, organic matter, water, &c.	18·36
		1002·22

	Constituents.	
Soluble in cold water.	Water	77·00
	Sulphuric acid	106·54
	Oxalic acid	55·63
	Phosphoric acid	23·10
	Hydrochloric acid	20·76
	Chlorine	192·22
	Soda	136·93
	Sodium	114·52
	Potash	28·27
	Potassium	21·91
	Ammonia	9·54
	Organic matter and combined water	25·53
Soluble in boiling water.	Lime	0·60
	Magnesia	0·18
	Phosphoric acid	0·66
	Organic matter and water	7·90
	Ammonia	0·15
Insoluble in water.	Sand, &c.	4·20
	Oxide of iron and alumina	1·50
	Lime	71·63
	Magnesia	9·21
	Phosphoric acid	76·09
	Organic matter, humus, &c.	18·36
		1002·43

On comparing the results of these five analyses, the extreme variableness of the composition of guano is the first thing that demands attention; no two samples resemble each other: in one, potash salts, abundance of urate of ammonia, with free uric acid exist; in another, the salts of the mixed alkalies are present, but the soda salts in far larger proportion than those of potash, and the amount of urate of ammonia diminished from about 17 to 2 per cent.; here also free uric acid is absent; in another instance of ordinary guano, No. 4, no uric acid whatever is present, and this specimen contains a large proportion of sand. The amount of ammonia also varies very considerably in this description of guano, and even the proportion of those salts which are common to both seldom bear any relation to each other. The state of combination in which the phosphate of lime occurs is also dissimilar; that of sample No. 1 apparently existing wholly as bone-phosphate, whilst that of No. 2 is a mixture of the neutral with the subsesquiphosphate of lime: instances of dissimilarity may readily be multiplied by a glance at the results of these two analyses, the resemblance to each other being for the most part confined to the existence of some similar salts in both cases.

Then, again, the samples of concrete guano differ not merely from the common guano, Nos. 1, 2, 3 and 4, but also widely from each other; sample No. 5, concrete guano, containing large proportions of sulphate of soda and oxalate of lime, no uric acid, and but a very small quantity, when compared to any of the other samples, of phosphate of lime—this existing in this specimen as bone-phosphate; whilst the other kind of concrete guano, No. 6, affords very small quantities of soluble substances, the merest trace of ammonia salts, and consists almost entirely of water and phosphate of lime. The constitution of this salt again varies from that which exists in the specimen No. 5, being chiefly neutral phosphate instead of the bone-phosphate. The saline guano is the very opposite of this last description; the larger proportion consisting of soda salts and others soluble in water: here also the ammoniacal salts are almost absent, whilst common salt, a substance existing in comparatively small quantities in the other samples, and totally absent in two of them, is by far its most prevalent constituent.

Can we then wonder that such widely differing results should have been obtained by various farmers and experimentalists who have used the substance termed guano; even when its application has taken place under almost identical circumstances, as respects quality of land, description of crop, time of application, &c. &c., and differing only in the guano used by either party

being obtained through different sources? Putting aside all considerations of the mode of application to the soil, it is obvious that the effects of such manures must vary almost as widely as their composition; and that whilst the employment of such guano as No. 1, or even No. 2, would be in all probability attended with highly successful results, the use of the others, or even of these mixed with several lumps of Nos. 5, 6 and 7, would, on the contrary, completely disappoint the expectations of the agriculturist, and probably in some cases, especially where such a kind as No. 7 exists in quantity, or has deliquesced and been absorbed by the other portions of the guano, its application would be attended with positive injury.

The analyses of the ordinary guano detailed in this paper do not differ so considerably from Voelckel's analysis in composition, and the salts which they respectively contain, as to render many observations on this the most complete analysis I have met with necessary. In no one instance of the seven specimens of guano examined by me could I detect carbonate of ammonia in sufficient quantity to affect lime-water, although in two cases out of the seven, nitrate of barytes indicated a faint trace of this substance. The solutions in cold water were either neutral or slightly acid: these solutions distilled afforded a solution which was distinctly alkaline to test-paper, and contained a considerable quantity of ammonia, but it was in an uncombined state, not as carbonate; the residual solution in the retort subsequent to distillation was markedly acid, so that this ammonia arose from the decomposition of the phosphate of ammonia by boiling the solution containing it. Some portions of guano, gently dried and then sublimed, gave off ammoniacal fumes, and a white sublimate from the oxalate, muriate and other ammonia salts, but the sublimate contained no carbonate of ammonia. In this respect my results differ from those of Girardin, Bidard and some others, who describe carbonate of ammonia to exist in considerable quantities in the South American guano analysed by them. May they not have assumed that the ammonia liberated by heat existed as carbonate, as I did myself until these analyses obliged me experimentally to determine the question? Carbonate of ammonia is a substance, which, considering the composition of guano, does not appear unlikely to be produced; so that whilst I admit the possibility and even the probability of its presence on these grounds, yet experiment on seven distinct samples shows that it is absent.

The existence of the free uric acid which separated from the solution in boiling water of No. 1, may be questioned as

to whether it ought not to be considered as a product arising from the decomposition of a portion of urate of ammonia by the presence of a stronger acid, rather than as existing in the specimen of guano in an uncombined state. This I cannot consider to have been the case; for although, like the other solutions made by boiling water, it was faintly acid, yet in No. 2 no free uric acid was discovered, although the urate of ammonia in that specimen existed under precisely the same circumstances as in the analysis of the first sample; and if uric acid had been evolved in the first instance from its combination with ammonia, this salt surely ought not to have escaped decomposition in the second case. I am therefore induced to consider it as highly probable that, when the dung of which guano is composed is freshly deposited, the uric acid which it contains is not wholly in a state of combination with ammonia, but that a portion exists as free uric acid.

I must now allude to the production of the oxalate of ammonia which is so constantly found in guano, being compelled on this point to differ with Dr. Fownes.

I am no friend to the hypothetical deductions which are now so constantly employed in organic chemistry. They may have their uses in leading the experimenter to the selection of the right path and the proper mode of investigating organized substances; but the abuses they are apt to engender, too often, I fear, more than counterbalance their advantages. Instances of the elevation of hypothesis to the rank and consideration due to ascertained and undoubted facts, and the erection of other theories upon the first hypothesis, are to be found thickly strewn throughout nearly every chemical publication of the present day; nor are the works of some of the most distinguished chemists free from this objection, but rather might be referred to as furnishing the most flagrant instances of this indulgence of a luxuriant imagination. In accordance with this usage, the sole requisite conditions to produce any given organic compound which may be known or imagined to exist, is to commence with a something which need contain but two elements, carbon and azote, and these are almost superfluous; add to this substance the oxygen of the atmosphere and water, as much as may be sufficient, liberate hydrogen, ammonia, oxygen, carbonic acid or azote, as may be necessary, and there is the substance sought for—*on paper*.

To return, however, to the formation of the oxalate of ammonia: it must, I presume, be formed from the urate of ammonia, because guano does not contain any other substance, except by such a process as is detailed above, which can produce it; in this, I believe, all chemists are agreed.

Now Dr. Fownes supposes that the uric acid of the urate of ammonia combines with eight equivalents of water and two of oxygen from the air, and produces four equivalents of oxalate of ammonia and two of carbonic acid, which of course unites, although it is not so stated in the note I refer to*, with the equivalent of ammonia before combined with the uric acid, producing the bicarbonate of ammonia, not the most volatile nor soluble of its salts, and which, if formed, surely ought to be found in every sample of guano. Now various specimens of guano have been examined, seven in number, in what we may suppose to be all the progressive stages of this conversion of the urate into the oxalate of ammonia; one containing uric acid, urate of ammonia and oxalate of ammonia; a second containing the two salts only; and others in which the uric acid and urate of ammonia have wholly disappeared, and oxalate of ammonia alone remains: yet in no one of these specimens of the guano has the substance, bicarbonate of ammonia, which is required by Dr. Fownes's theory, been detected; its presence would not necessarily have proved the theory to be correct, as it might fairly and possibly be attributed to the decay of azotized animal matter: but I respectfully submit that the absence of this ammoniacal salt proves this hypothesis of the conversion of urate into oxalate of ammonia to be erroneous. After the opinions I have uttered respecting the employment of hypothetical deductions, it is certainly vastly inconsistent on my part to have recourse to them, but it will tend to prove the truth of my former remarks on the readiness with which a theory in organic chemistry may be constructed, when no inconvenient nor insurmountable facts are opposed to it. In detailing this theory of the conversion of the urate into the oxalate of ammonia, I am more than indifferent to its fate; for gladly will I lend a helping hand to put an extinguisher upon it, if one based upon the actual and experimental conversion of the one salt into the other, a result I have endeavoured in vain to effect, is propounded.

Since Coindet's observation, that the uric acid in the excrement of birds existed as binurate of ammonia, the equivalent number of uric acid seems by general consent to have been doubled, so that this acid salt, according to Coindet's view, must now be considered as neutral urate of ammonia. Like Dr. Fownes's, my hypothesis of this conversion is an absorption of water and very slight oxidation, differing from his only in the proportions of these convenient substances, and in the conversion of the urate into the oxalate of ammonia without the formation of carbonate of ammonia or any other secondary

* Memoirs of Chemical Society, part 3, p. 38.

products,—one equivalent of urate of ammonia combining with 8 equivalents of water and 1 of oxygen, and producing 5 equivalents of oxalate of ammonia.

Uric acid . .	$C^{10}N^4H^4O^6$	Oxalic acid .	C^2O^3
Ammonia . .	NH^3	Ammonia . .	NH^3
	$C^{10}N^5H^7O^6$		$C^2O^3NH^3$
Water, 8 eqs.	H^8O^8		5
Oxygen, 1 eq.	O		$C^{10}O^{15}N^5H^{15}$
	$C^{10}N^5H^{15}O^{15}$		

This theory has simplicity to recommend it, and is in accordance with observed facts, so far as they go; but after all it is merely hypothesis, and rests upon no experimental proof whatever; and I neither have faith in it myself, nor recommend it as worthy of credence by others. A more legitimate subject of speculation than the mode in which the oxalate of ammonia found in guano is produced, is the origin of guano itself and of its varieties. The large lumps found in the bags of guano, which I have termed "concrete guano," appear to me to have been taken from the oldest portions of the beds of this substance, and in which decay of the organic salts and animal substances has proceeded further than in common guano, and that concrete guano is merely ordinary guano in an advanced stage of decay agglomerated by pressure and long contact. This remark applies chiefly to sample No. 5. I consider it probable that samples 6 and 7 are formed from the action of sea water on a bed of guano somewhat deficient in ammonia salts and containing no urate of ammonia; in short, one of the oldest beds on the lower ledges of the coast and rocks. The spray of the sea falling upon a bed of guano in this position mixes with it, the insoluble portions subside in regular horizontal strata, which again dries and hardens, giving rise to the formation of masses consisting chiefly of insoluble substances, as in the specimen No. 6, whilst the solution collecting in the crevices and hollows is subsequently dried by evaporation in a dry atmosphere, and forms the saline guano, No. 7, in which common salt so greatly predominates, the oxalate of ammonia being converted by double decomposition into oxalate of soda and muriate of ammonia; the disappearance of the larger portion of the latter salt I can only account for by its well-known tendency, when in a damp state, as existing as a saturated solution, to creep over the sides of the vessels which contain it, by which means it may have separated itself from the sea-water solution previously alluded to before that became quite solid and dry, and thus extending itself over the ledges of rock, assisted in its progress by noc-

turnal dews, has been finally washed away by the sea-water. This is rather an unsatisfactory mode of accounting for the absence of the muriate of ammonia, which from what we know of guano, and the existence of oxalate of soda in the saline guano, we may fairly conclude must have been formed, bu which in the sample I have examined contains but little more than one equivalent of muriate of ammonia to three of oxalate of soda, so that nearly two equivalents have disappeared.

As to the respective hypotheses of the coprolitic or recent nature of these deposits, I have never held but one opinion, the one I believe generally entertained, that this manure is deposited by sea-fowl inhabiting coasts where no rain falls, and which consequently is never washed away. This view is supported by all ancient and most modern authorities, and has recently received additional confirmation from Mr. Teschemacher of Boston, who has presented specimens of Peruvian guano to the Philosophical Society of that town, containing *feathers*; and after quoting the accounts given by the old Portuguese historian respecting the formation and preservation of this manure, very justly remarks, that the beds of the greatest thickness hitherto observed might, without any extravagant calculation, and at the rate only of two to three inches a year, or less, be deposited in about three thousand years; whilst the theory of its coprolitic origin not merely requires a considerable exercise of the imagination, but is opposed by the direct testimony of eye-witnesses.

P.S. The May Number of the Philosophical Magazine, which has just come into my hands, contains an analysis of African guano by our Foreign Secretary, Mr. E. F. Teschemacher, in which he finds humic acid to exist in a soluble state in the African specimen, but no urate of ammonia. The humus described to exist in the Peruvian specimens analysed by me was extracted by dilute potash from the residue insoluble in water; and if it be true humus, and it possesses all the characters assigned to that substance, the South American varies from the African guano, amongst other differences, in containing uncombined humus.

CXI. *Observations upon the Decomposition of the Double Cyanides by an Electric Current.* By Mr. James Napier.

FOR some time past I have considered that there were phænomena presenting themselves in my daily operations of depositing metals by a galvanic current of sufficient scientific interest to warrant their being collected and given in detail to

this Society. In anticipation of doing so, I carefully noted down what seemed most interesting, in hopes of being prepared to give them as a short series of papers next session: I say series, because so far as I have observed, all the double cyanides, even when they have the same constitution, do not comport themselves in the same manner, giving rise to different results, all of which could not be given in the compass of one paper. But these anticipations have been somewhat changed by the circumstance, that a paper upon a similar subject has lately been read by Prof. Daniell to the Royal Society. The facts brought forward in that paper are as yet unknown to me, further than that certain metals are not transferred from one pole of the galvanic circuit to the other by means of the current; this is one of the facts to which my attention has been directed for a long time, and I am induced to bring this paper forward to-night, not with any desire of sharing the honours due to the discovery, but in hopes that, while noticing this in connection with other facts which I hope to have the honour of laying before you next session, I may have a little more claim upon your attention, from its having been original on my part.

The present paper is more particularly devoted to cyanide of potassium and silver,—a double salt of general use in electro-metallurgical operations, and one of a class eminently fitted to exhibit some of the most interesting facts in connection with electrical decompositions. It is known to those engaged in the deposition of silver from this salt, that if it be used pure, or in a neutral state, with a positive electrode of silver, no deposition of metal is obtained unless a battery of great power be used; but if a little cyanide of potassium be added to the solution, a very weak current of electricity is sufficient to give a deposit. The usual explanation of these facts is, that pure or neutral cyanide of potassium and silver is a bad conductor of electricity, and that the addition of free cyanide of potassium gives it conducting power, either as being the conducting medium, or by a kind of disposing influence which it imparts to the salt decomposed. That one fluid imparts such an influence to another I need hardly say is absurd; and it is well known that the conducting medium in any fluid is the substance decomposed. It is certain that the free cyanide of potassium, which is added with the idea of giving conduction, is not decomposed. The question then occurs, what part does it take in these operations? I have observed that, whilst endeavouring to deposit from the neutral salt, the positive electrode, although brightly polished previous to being put into the solution, instantly assumed a chalky aspect. It appeared

probable that this was owing to the formation of cyanide of silver, which, being insoluble in the neutral salt, obstructed the current of electricity by its coating. To prove this, I placed a quantity of crystallized cyanide of potassium and silver, dissolved in water, in a long shallow vessel, kept the two electrodes at a considerable distance apart, and connected them with a battery of 20 pairs of plates for forty-eight hours: there was a considerable deposit of silver upon the cathode, the solution around it was strongly alkaline, and the precipitate formed by adding a drop of nitrate of silver was easily redissolved; whilst that part of the solution round the anode remained neutral, the anode was covered over with a grayish-white powder, which being washed exhibited every character of cyanide of silver. The use of the addition of free cyanide of potassium to the silver solution was now evident, not to facilitate the passage of the current, but to dissolve the cyanide of silver formed upon the electrode. To make this the more certain, I dissolved 2 equivalents of the cyanide of potassium, or twice 200 grains, and put them into a vessel divided by a porous diaphragm: into the division in which the anode was placed I put an equivalent of cyanide of potassium, or 66 grains; the electrodes being previously weighed, were connected with a battery of 4 pairs, deposition immediately took place; the current was continued for twelve hours; towards the end of the operation hydrogen gas began to be evolved from the cathode, and a powder to appear upon the anode; the experiment was then stopped; the anode being washed and weighed indicated a loss of 108·7 grains; the solution in which it was placed was neutral, and on being evaporated and fused yielded 214·3 grains of silver; the cathode had gained 107·4 grains in weight; the solution in which it was placed had a powerful alkaline reaction, smelled strongly of hydrocyanic acid, and on being tested scarcely indicated the presence of silver. This last circumstance attracted particular attention, and induced me to repeat the experiment under various modifications, also with gold, copper and zinc, all of which gave similar results.

Another question suggested itself in connection with the decomposition of cyanide of potassium and silver, namely, does the cyanide of potassium which is in union with the cyanide of silver take any part in these decompositions? To determine this, the experiment just detailed was repeated, taking care to reduce the power of the current of electricity when any indication of gas was perceived at the cathode; when the experiment was completed, the solution containing the negative electrode was tested for the quantity of cyanide of

potassium by nitrate of silver, it indicated 67·4 grains, which is more than an equivalent, independent of loss by decomposition. The reason of the cyanide of potassium being more than the equivalent, is from that invariable endosmose which takes place when a current of electricity is passing which is in the direction of the negative division. From this experiment it appears that the cyanide of potassium which is combined with the cyanide of silver undergoes no change by the electric current, if it be properly regulated to the condition of the solution, so long as cyanide of silver is present: this exhibits beautifully the different conducting power of the two salts, and so long as there is not more electricity than the best conductor can transmit, it will pass through it in preference to any other salt mixed with it, although such other may be also an excellent conductor. But when the current is more than the best conductor will transmit, it passes through the next best present, which accordingly suffers decomposition; so that in the case of cyanide of potassium and silver, when the current is more than the cyanide of silver will transmit, the cyanide of potassium is also decomposed, so that two proportionals of cyanogen pass to the positive electrode, which being dissolved increases the quantity of silver in the solution, while potassium is liberated at the negative electrode, decomposing water with the escape of hydrogen gas.

If platinum electrodes be used there is no necessity for adding free cyanide of potassium, the pure solution being decomposed by a weak current, and the cyanogen liberated at the anode is absorbed by the solution, turning it dark brown and leaving a slight blackish precipitate, probably paracyanogen; this has been already observed by Professor Faraday in cyanide of potassium alone; but if the current be increased to 7 or 8 pairs of plates, oxygen gas is evolved from the anode, and cyanide of silver is precipitated upon its surface, the cyanogen being decomposed forming ammonia and probably formic acid, which latter decomposes the cyanide of potassium combined with the cyanide of silver, forming hydrocyanic acid and formiate of potash, the cyanide of silver being precipitated. Several other reactions take place, but my experiments are not yet sufficiently numerous to allow of my venturing upon a description of them in this paper.

It is evident, therefore, that the cyanide of potassium and silver in a neutral state is a most excellent conductor of electricity. A little cyanide of potassium added does however facilitate its decomposition; and it is remarkable that when the cyanide of potassium added is in such proportion as to form a compound having two equivalents of cyanide of potas-

sium to one of cyanide of silver, it is probably the most easily decomposed substance that we have. I have deposited silver from it easily with one square inch of copper and zinc immersed in water, the solution being at a temperature of 75°.

Another question suggested itself in connection with this salt, namely, the manner in which the cyanogen is transferred from the negative to the positive electrode, whether it travels direct, or is transmitted from particle to particle. Probably this has been answered satisfactorily long ago by other experimenters; but this being a salt eminently fitted to determine this question, I made the following experiment:—Into one division of the decomposition cell, a solution of pure cyanide of potassium and silver was introduced, and into the other division a neutral solution of chloride of potassium. By this arrangement, I considered that, if the cyanogen travelled direct, cyanide of silver should be formed upon the positive electrode which was immersed in the chloride of potassium; and if it was transmitted from particle to particle, chloride of silver would be deposited upon the pole and cyanide of potassium formed in the solution. The experiment verified this last supposition; after a current had passed through the solution for nearly eight hours the positive electrode was completely encased in a horny crust of considerable flexibility, which was not soluble in strong boiling nitric acid nor in hot sulphuric acid, and did not give off fumes of hydrocyanic acid on the addition of muriatic acid. 25 grains gave 18·6 of silver, which with the previous experiments is sufficient to prove the substance to be chloride of silver; the solution had the smell of cyanide of potassium, which had dissolved or decomposed a portion of the chloride of silver it held in solution.

May 20, 1844.—Thomas Graham, Esq., Vice-President, in the Chair.

Specimens of Tartaric Acid, Quadroxalate of Potash and Bicarbonate of Ammonia were presented by Mr. Scanlan, and a Specimen of crystallized Tin by Mr. Chabot to the Society's Museum.

John Middleton, Esq. and Charles Davy, Esq. were duly elected Members of the Society.

The following communications were then read, after which the Society adjourned to the evening of the 4th of November.

CXII. *Abstract of a Letter from* H. B. Leeson, *M.D., on the Preparation of Fluoride of Iodine.*

THE fluoride of iodine, of which I presented a specimen to the Chemical Society on the 1st of April, was prepared by passing the gas generated from 1 part of peroxide of man-

ganese, 3 of pure fluor spar, and 6 of concentrated sulphuric acid through water, in which the iodine was diffused (contained in a glass vessel) until the whole of the iodine was taken up. A leaden retort and conducting tube was made use of. The leaden tube did not appear to be acted upon, neither could any trace of lead be detected in the product, which gradually deposits in crystalline scales, very similar in appearance to those of iodide of lead. Fluoride of bromine was prepared in a similar manner, but did not yield a crystalline deposit, being very soluble in water. The latter answers extremely well for the Daguerreotype, giving instantaneous pictures, but I cannot at present decide that it is superior to bromine alone.

I hope when the Society reassembles to furnish them with a more detailed account of these compounds.

CXIII. *On the Composition of Narcotine, and some of its products of Decomposition by the action of Bichloride of Platinum.* By J. Blyth, *M.D.*

NARCOTINE has been analysed by M. Liebig, Pelletier and Regnault. From these analyses, although agreeing in the relative proportion of the constituents, different formulæ have been deduced, arising from the dissimilar atomic weights admitted by each.

The original method adopted by M. Liebig for determining the atomic weight, was by saturating a known portion of narcotine with hydrochloric acid gas, and after expelling the excess of acid in a drying apparatus by a current of air, the increase of weight of the original substance indicated the amount of acid which had entered into combination. The number found by this method was 4799 *.

The analysis gave in a hundred parts—

Carbon	65·00
Hydrogen	5·50
Nitrogen	2·51
Oxygen	26·99

The formula deduced from which was $C_{40}\ H_{20}\ N\ O_{12}$.

M. Regnault, in a later research on the constitution of the organic alkalies, investigated very carefully the atomic weight and composition of narcotine †. The plan pursued by him was the same as that employed by M. Liebig. Different portions of narcotine saturated with hydrochloric acid gas

* *Annalen der Pharmacie*, band vi. p. 35.

† *Ann. de Chim. et de Phys.*, t. lxviii. p. 139.

gave 5139, 5127·6, 5253 as the atomic weights. The composition after combustion expressed in 100 parts was found to be

	I.	II.	III.
Carbon . .	64·91	65·30	64·98
Hydrogen .	5·96	5·99	5·73
Nitrogen . .	3·46	3·52	
Oxygen . .	25·67	25·19	

Taking the mean of the first two of the above weights, 5139, 5127·6, which also agreed nearly with the number 5100·3 obtained by Robiquet from hydrochlorate of narcotine crystallized from alcohol, M. Regnault constructed the formula C_{44} H_{23} N O_{13}.

		Calculated.
C_{44} =	3363·4	65·60
H_{23} =	287	5·60
N =	177	3·45
O_{13} =	1300	25·35
	5127·4	100·00

More lately M. Liebig has examined the atomic weight and constitution of many of the organic alkalies by a new method proposed by himself*. These bases in most cases form insoluble double salts with bichloride of platinum, which in their constitution are exactly analogous to the bichloride of platinum and ammonium; one equivalent of bichloride of platinum being united to one equivalent of the hydrochlorate of the base. From the quantity of metallic platinum left after combustion, the atomic weight can be easily calculated.

The double salt of platinum and narcotine gave in 100 parts 14·508 and 14·64 of metallic platinum. The atomic weights corresponding to these are 5930 and 5780. The formula calculated by M. Liebig from these numbers with the analysis formerly made, was C_{48} H_{24} N O_{15}.

The following table exhibits the great difference in the composition of narcotine admitted by M. Liebig, Regnault and Pelletier, although the results of the analyses are nearly similar.

Atomic weight found.

Liebig.		Regnault.	Robiquet.
Old.	New.		
4799	5930	5139	5100·3
	5780	5127·6	
		5253	

* *Annalen der Pharmacie*, band xxvi. s. 45.

Composition in 100 *parts.*

	Liebig.	Regnault.		Pelletier.
Carbon .	65·00	64·91	65·30	65·16
Hydrogen	5·50	5·96	5·99	5·45
Nitrogen .	2·51	3·46	3·52	4·31
Oxygen .	26·99	25·67	25·25	25·08

Formulæ deduced.

Liebig.		Regnault.	Pelletier.
Old.	New.		
C_{40}	C_{48}	C_{44}	C_{34}
H_{20}	H_{24}	H_{23}	H_{17}
N	N	N	N
O_{12}	O_{15}	O_{13}	O_{10}

These widely-differing formulæ, calculated from analyses agreeing so nearly, made it particularly necessary to determine anew the atomic weight. I undertook the subject at the request of Professor Liebig, to whose valuable assistance in the further prosecution of my investigation I consider myself much indebted.

A. *Composition of Narcotine.*

The determination of the platinum in the double salt of that metal was the method adopted in my investigations. The first attempts gave constantly varying results; the per-centage of platinum found being 15·441, 16·7, 14·303, 14·84, 16·1, 16·6. The following per-centages of platinum obtained by my friend Dr. A. W. Hofmann were kindly communicated to me, 16·63, 16·49, 16·77. From these numbers it appeared that the atomic weight of narcotine could not be deduced accurately from its platinum double salt. Upon carefully repeating the experiments, it was found that this difference arose from two sources of error. The first is, that the platinum double salt is decomposed if submitted to washing for too long a time. A portion of the double salt, already freed from the excess of the bichloride of platinum employed to precipitate it, was thrown on a filter and submitted to further washing. The fluid passed through of a pale greenish colour, from which, on adding a solution of hydrochlorate of narcotine, a precipitate was obtained.

I. 0·571 grm. of this precipitate, carefully dried, gave on combustion 0·09 metallic platinum = 15·76 per cent.

II. 0·996 of the salt still remaining on the filter gave platinum 0·1538 = 15·441 per cent.

The second source of error lay in the action of the bichlo-

ride of platinum under the influence of a temperature much below 100° C. For the purpose of causing the precipitate of the double salt to settle more quickly in an agglomerated form, it was placed in a water-bath and heated much below the boiling point. The salt speedily collected at the bottom of the vessel in a half melted state, and the supernatant fluid became of an orange colour, from which, on filtering and cooling, large dark red crystals mingled with long white needles were deposited. The same fact was observed on boiling a portion of platinchloride of narcotine in a larger quantity of water, with the view of getting it for analysis in a more distinctly crystalline form from its watery solution. On cooling the greater portion again precipitated. The mother-liquor, also of an orange colour, upon evaporation gave the same red crystals mingled with the white. From a portion of the former collected and burned, the quantity of metallic platinum obtained per cent. was 22·45. The white crystals were found to be identical with opianic acid, already obtained by M. Liebig and Wöhler from narcotine, by the action of peroxide of manganese and sulphuric acid.

It is probable that in determining the atomic weight of narcotine from its platinum double salt, the error in most cases arose from the employment of too great an excess of the bichloride of platinum for precipitation, under the influence of heat. Bichloride of platinum under these circumstances acts just as any other oxidizing agent, being itself reduced to the state of protochloride. In those instances in which the per-centage of platinum is given high, it is likely that the salt analysed was mixed with a portion of these red crystals containing above 22 per cent. of platinum.

To avoid these two sources of error, pure narcotine was dissolved in dilute hydrochloric acid, and to the cold solution just so much bichloride of platinum was added as was sufficient for the precipitation. After removal of the fluid by the Bramah press, the dry mass was pounded, again thrown on a filter and washed with a small portion of distilled water. The salt thus prepared should be dried at a temperature below 100° C. In the following analyses different preparations were employed.

I. 0·9905 grm. gave platinum 0·1585 = 16·00 per cent.; atomic weight calculated = 5135.

II. 0·9313 grm. gave platinum 0·1486 = 15·95 per cent.; atomic weight = 5159.

III. 0·907 grm. gave platinum 0·142 = 15·65 per cent.; atomic weight = 5304·67.

IV. 0·947 grm. gave platinum 0·149 = 15·73 per cent.; atomic weight = 5265·83.

A salt carefully prepared by Dr. A. W. Hofmann gave from

V. 0·7617 grm. 0·1208 of metallic platinum = 15·85 per cent.; atomic weight calculated from this = 5208.

VI. 0·6272 grm. gave platinum 0·0991 = 15·8 per cent.; atomic weight = 5232.

The atomic weight adopted from the mean of the last three analyses, which were most carefully made, is 5235. With this number I now attempted to construct a formula from my own analyses of the double platinum salt, and from those of narcotine itself made by M. Liebig, Pelletier and Regnault.

I. 0·6535 grm. platinchloride of narcotine, burned with chromate of lead, gave carbonic acid 1·0477, water 0·2455.

II. 0·4025 grm. gave carbonic acid 0·643, water 0·156.

These correspond in the hundred parts to

	I.	II.
Carbon	43·72	43·56
Hydrogen	4·17	4·30

From which the following formula is deduced:—

	Calculated.	Found.
C_{46} = 3450	43·70	
H_{62} = 325	4·10	
N = 177		
O_{14} = 1400		
Pt = 1233·5	15·81	15·80
Cl_3 = 1327·9		
7913·4	atomic weight of double salt.	
2573·9	= HCl + $PtCl_2$.	
5339·5	= calculated atomic weight of narcotine.	

Formula of narcotine taken from the above:

$$C_{46}\ H_{25}\ N\ O_{14}.$$

The same formula is deduced from the analyses of M. Liebig, Regnault, &c.

The atomic weight of carbon employed in this memoir being 75, gives in 100 parts for the analyses of these chemists—

	Liebig.	Regnault.		A. W. Hofmann.
Carbon .	64·09	64·01	64·50	64·53*
Hydrogen	5·50	5·96	5·97	6·21
Nitrogen .	2·51	3·46	3·52	3·30
Oxygen .	27·9	26·57	26·01	25·96
	100·00	100·00	100 00	100·00

* By this analysis the following numbers were found:—
0·4649 grm. narcotine gave CO_2 = 1·100, water = 0 26.
0·548 grm. do. gave 0·289 platinchloride ammonium.
0·4697 grm. do. gave 0·219 ditto.

Formula calculated from these numbers—

$$C_{46}\,H_{25}\,N\,O_{14}.$$

		Calculated.
C_{46}	= 3450	64·61
H_{25}	= 312·5	5·85
N	= 177	3·31
O_{14}	= 1400	26·23
	5339·5	100·00

B. *Products of Decomposition.*

I endeavoured by following out the products of decomposition produced by bichloride of platinum to see how far the analyses of these bodies would support the formula given above for narcotine.

An ounce and a half of narcotine, dissolved in dilute hydrochloric acid, was precipitated by bichloride of platinum, and formed into a thin paste by the addition of distilled water. A large excess of bichloride of platinum, amounting fully to the quantity used for precipitation, was then added, and the whole heated in a basin over a fire. Upon the mass becoming blood-warm, the colour of the fluid portion changed from yellow to orange, and traces of opianic acid were formed. On further elevation of the temperature, but considerably before arriving at the boiling point, the fluid assumed a still darker orange colour, the platinum double salt melted, and a quantity of opianic acid made its appearance. To ensure an uniform product ebullition was continued for half an hour, at the end of which time the opianic acid was re-dissolved and the surface of the liquid became covered with dark red crystals. These were separated by rapid filtration, and washed with hot distilled water to free them from all traces of the accompanying acid. The acid was deposited in fine needles from the filtered liquid on cooling. The mother-liquor, decanted and further evaporated, gave another portion mingled with long crystals of a rhombic prismatic form. These being more soluble than the opianic acid, were redissolved and separated by filtration.

The fluid evaporated to one-tenth its original quantity became of a very dark brown colour, gave off hydrochloric acid abundantly, and deposited large colourless crystals in the form of rhombohedrons, which upon resolution and rapid crystallization assumed their original figure of long rhombic prisms.

Whilst proceeding with my investigation, Prof. Liebig informed me that he had received a communication from Prof. Wöhler of Gottingen, stating that in studying the products of the decomposition of narcotine by the action of peroxide of

manganese and sulphuric acid, on which he had for some time been engaged, he had already produced, among other results, some of the same compounds as those derived by me through the agency of the bichloride of platinum. I have therefore confined my investigation merely to the study of those substances I had already obtained, and have adopted the names proposed by Prof. Wöhler for those of them which had been also found by him.

The red platinum salt, platinchloride of cotarnin, crystallizes in large red, six-sided prisms, which are slightly soluble in hot water, and can be boiled in ammonia without suffering decomposition.

I. 2·679 grms. of this salt dried at 100° C. gave of metallic platinum 0·614 = 22·91 per cent.: from which the calculated atomic weight is 2808·04.

II. 0·743 grm. of the same preparation gave platinum 0·17 = 22·88 per cent.; atomic weight = 2817·17.

III. 0·997 grm. of a different preparation gave platinum 0·23 = 23·06 per cent; atomic weight = 2773.

The combustion with chromate of lead gave the following numbers:—

1·1142 grm. dried at 100° C. gave carbonic acid 1·4055, water 0·334.

	Per cent.
Carbon	= 34·4
Hydrogen	= 3·33

Admitting only one equivalent of nitrogen to be present, the formula deduced from these numbers is $C_{25}\,H_{13}\,NO_6$, HCl + Pt Cl_2, as is apparent from the results calculated and found.

		Calculated.	Found.	
C_{25}	= 1875	34·7	34·4	
H_{14}	= 175	3·24	3·33	
N	= 177			
O_6	= 600			
Pt	= 1233·5	22·89	22·88	22·91
Cl_3	= 1328			
	5388·5 = atomic weight of the platinum salt.			

Another analysis of this double salt, prepared directly from the base, will be given afterwards.

From the platinchloride of cotarnin the base can be easily separated by boiling in hydrosulphuret of ammonia. The method I pursued was the following:—The salt was first boiled in ammonia, in which it experienced no change, and while hot acted on by a stream of sulphuretted hydrogen; decomposition rapidly took place. The residue left, on carefully evaporating the mixture to dryness on the water-bath, was treated

with distilled water, to which hydrochloric acid was added till the reaction was feebly acid, in order to decompose the soluble double salt of bisulphuret of platinum and ammonium formed during the reduction of the platinchloride of cotarnin. On filtering, a fluid passed through of a dark brown colour, from which, on the addition of caustic potash, the base was precipitated. The supernatant fluid, decanted off and evaporated till no trace of ammonia was left, gave another portion of base which had been held in solution by that alkali. The whole precipitate was again dissolved in dilute hydrochloric acid, boiled with animal charcoal, and after filtration again precipitated by potash.

Cotarnin when pure presents itself in the form of stellated groups of colourless needles. It melts at 100° C. into a brown mass, without suffering decomposition, and loses about 7 per cent. of its weight. It is slightly soluble in cold, but more so in hot water. Alcohol forms with it a dark brown solution, from which the cotarnin cannot again be obtained in a crystalline form. In ammonia and æther it is readily dissolved, but is insoluble in potash. Strong nitric acid forms with it a dark red solution. The persalts of iron do not affect its colour. Its watery solution precipitates salts of copper and of the protoxide of iron.

The salts of cotarnin are obtained by dissolving this base in the dilute acids; they are extremely soluble.

0·1807 grm. of cotarnin, dried at 100° C. and burned with peroxide of copper, gave carbonic acid 0·437, water 0·1040.

	Per cent.
Carbon	=65·95
Hydrogen	= 6·39

These numbers correspond to those calculated from the formula given by the platinum salt.

		Calculated.
C_{25}	=1875	66·61
H_{13}	= 162·5	5·77
N	= 177	
O_6	= 600	
	2814·5 = calculated atomic weight.	

The difference between the carbon found and calculated arises partly from the small quantity of substance employed in the analysis, a second combustion was made of a larger portion of crystallized cotarnin dried over sulphuric acid.

0·0357 grm. of crystallized cotarnin dried over sulphuric acid gave carbonic acid 0·756, water 0·193.

0·5852 grm. of the same, for the determination of nitro-

gen, gave, according to the method of Will and Varrentrapp, 0·224 grm. of metallic platinum.

These numbers correspond to the formula $C_{25}\ H_{15}\ NO_8$.

		Calculated.	Found.
C_{25}	= 1875	61·68	61·41
H_{15}	= 187·5	6·16	6·38
N	= 177	5·82	5·52
O_8	= 800	26·34	26·69
	3039·5	100·00	100·00

The formula of crystallized cotarnin deduced from this is $C_{25}\ H_{13}\ N\ O_6 + 2Aq$, which is satisfactorily confirmed by a direct determination of the water of crystallization.

0·2463 grm. of crystallized cotarnin dried at 100° C. and completely melted lost 0·0185 grm. = 7·51 per cent.

0·2522 grm. lost 0·0182 grm. = 7·216 per cent.

	Calculated.	Found.
1 equiv. of anhydrous cotarnin = 2814·5		
2 equiv. of water . . . . = 225	7·44	7·51 7·216
1 equiv. of crystallized cotarnin = 3039·5		

Hydrochlorate of Cotarnin is formed by dissolving cotarnin in dilute hydrochloric acid. From this solution, by very long evaporation, the salt is obtained in long silky crystals, which are extremely soluble in water. With the bichlorides of mercury and gold it forms double salts, the colour of the latter being of a beautiful dark red.

I. 0·3215 grm. of this salt dried at 100° C. lost 0·049 grm. = 15·24 per cent.

II. 0·4577 grm. lost 0·0664 = 14·51 per cent.

III. 0·3907 grm. in beautiful crystals dried at 100° C. gave carbonic acid 0·8222 grm., water 0·203.

IV. 0·271 grm. gave water 0·139 grm.

These numbers give the following formula:—

$$C_{25}\ H_{13}\ N\ O_6,\ HCl + 5Aq.$$

		Calculated.	Found.
C_{25}	= 1875	57·36	57·39
H_{14}	= 175	5·35	5·69 5·77
N	= 177·04		
O_6	= 600		
Cl	= 442·65		
	3269·69		

	Calculated.	Found.
1 eq. of anhydrous hydroch. of cotarnin = 3269·69		
5 eq. of water . . . . . = 562·5	14·67	14·51 15·24
1 eq. of crystallized hydroch. of cotarnin = 3832·19		

I again prepared the platinum double salt directly from the base: this on precipitation is of a pale yellow, but by drying assumes its characteristic dark red colour.

0·9418 grm. gave 0·2165 grm. of metallic platinum:

0·3873 grm. burned with chromate of lead gave carbonic acid 0·4968, water 0·1273.

These numbers correspond in 100 parts to—

	Calculated.	Found.
Carbon	=34·90	34·98
Hydrogen	= 3·24	3·65
Platinum	=22·89	22·98

Opianic Acid.—This acid having been already examined by Prof. Liebig and Wöhler, I did not enter into its investigation.

I. 0·5755 grm. gave on combustion with peroxide of copper carbonic acid 1·208, water=0·250.

II. 0·504 grm. gave carbonic acid 1·0495, water=0·223.

	In 100 parts. I.	II.
Carbon	=57·24	56·79
Hydrogen	= 4·82	4·91
Oxygen	=37·94	38·30
	100·00	100·00

If the atomic weight 2567 given by M. Liebig and Wöhler* be taken as approximative, the formula of the crystallized acid will be—

		Calculated.
C_{20}	=1500	57·41
H_9	= 112·5	4·36
O_{10}	=1000	38·23
	2612·5	100·00

Prof. Liebig kindly informed me that the formula established by M. Wöhler, who had fully studied this acid, agreed exactly with this.

Hemipinic Acid.—This acid accompanies opianic acid in all the processes of the oxidation of narcotine. After removal of the latter acid from the mother-liquor, the hemipinic acid is obtained by slow evaporation. The fluid becomes of a dark orange colour, almost approaching to black, and gives off hydrochloric acid abundantly. If the evaporation has been spontaneous, the hemipinic acid crystallizes in large flat rhombohedrons, which on resolution and rapid crystallization assume the form of long rhombic prisms.

The crystals of this acid effloresce on exposure to the air.

* *Traité de Chémie Organique*, par M. Liebig, t. ii. p. 656.

It is more soluble in water than opianic acid, the solution having an acid reaction: alcohol and æther dissolve it readily.

From opianic acid it is distinguished by its forming insoluble salts with the oxides of lead, silver and peroxide of iron, all the salts of opianic acid being soluble. The hemipinate of the peroxide of iron is of a fine orange colour.

0·2505 grm. of the hemipinate of silver gave on combustion 0·1237 of metallic silver=49·38 per cent., from which the calculated atomic weight is 1285·4.

0·402 grm. of the same salt gave 3·1975 of metallic silver =49·12 per cent., corresponding atomic weight=1299·5.

0·338 grm. of crystallized hemipinic acid dried at 100° C. gave carbonic acid 0·656, water 0·1395.

The corresponding formula is—

		Calculated.	Found.
C_{10} =	750	53·09	52·93
H_5 =	62·5	4·42	4·58
O_6 =	600	42·49	42·49
	1412·5	100·00	100·00

An unfortunate accident deprived me of the means of giving the combustion analysis of a pure silver salt. The combustion of an impure specimen gave the following approximative results:—

0·4985 grm. of substance gave carbonic acid 0·5115 grm., water 0·90 grm.

These numbers express—

		Calculated.	Found.
C_{10} =	750	27·30	27·98
H_4 =	50	1·81	2·00
O_6 =	600		
Ag =	1351·6	49·12	49·12
		100·00	100·00

The formula of crystallized hemipinic acid deduced from these analyses is $HO + C_{10} H_4 O_5$, and the atomic weight of the anhydrous acid 1300.

From its formula it appeared to be a product of the oxidation of opianic acid. To establish this point, a portion of the latter was boiled in an excess of bichloride of platinum. The liquid, separated by filtration from the undecomposed opianic acid, which is deposited on cooling, and submitted to further evaporation, gave crystals of hemipinic acid.

Narcogenin.—Besides those bodies already mentioned, the oxidation of narcotine also produces a base which is intermediate between it and cotarnin. Its platinum salt was accidentally obtained by me in endeavouring to prepare platin-

chloride of cotarnin. The exact circumstances under which it alone is produced has not been accurately ascertained. In my experiments it has generally been accompanied by a small portion of platinchloride of cotarnin. It appears however to depend upon the excess of bichloride of platinum, with which platinchloride of narcotine is boiled. On employing a large excess, not a trace of this base is to be found; the products being platinchloride of cotarnin, opianic acid, and hemipinic acid. If, on the other hand, a very small excess of bichloride of platinum is used, scarcely any cotarnin is formed; the products being the new platinum compound, opianic and hemipinic acid. This double salt, for which I propose the name of platinchloride of narcogenin, crystallizes in long needles of a light orange colour, and is at once distinguished from the corresponding salt of cotarnin and narcotine by its colour and crystalline form, but more particularly by the action of ammonia. Upon the two latter salts this volatile alkali has no action, further than slightly darkening the platinchloride of narcotine, whilst platinchloride of narcogenin becomes paler on contact with it, and suffers complete decomposition by the application of heat.

I. 0·6455 grm. of platinchloride of narcogenin on combustion left metallic platinum 0·118 grm. = 18·03 per cent.; corresponding atomic weight of the platinum salt = 6841.

II. 0·6008 grm. gave platinum 0·1088 grm. = 18·10 per cent.; atomic weight = 6814.

III. 1·1735 grm. gave platinum 0·2105 grm. = 17·93 per cent.; atomic weight = 6879.

IV. 0·5803 grm. of another salt, which had been dissolved in boiling water and crystallized, gave platinum 0·1076 grm. = 18·54 per cent.; corresponding atomic weight = 6653.

The salts employed in the determination of these atomic weights were of different preparation. The following analyses are given rather as approximate than as accurate, on account of the difficulty of obtaining platinchloride of narcogenin quite free from other matters.

On combustion with chromate of lead,—

I. 0·390 grm. gave carbonic acid 0·584, water 0·140
II. 0·2665 ... ... 0·3955, ... 0·1002
III. 0·286 ... ... 0·4255, ... 0·109

	In 100 parts. I.	II.	III.
Carbon . .	40·83	40·47	40.57
Hydrogen .	3·98	4·12	4·23

These numbers correspond to the following formula:—

		Calculated.	Found.
C_{36}	=2700	40·38	40·62 mean.
H_{20}	= 250	3·73	4·11 ...
N	= 177		
O_{10}	=1000		
Pt	=1233	18·44	18·15 ...
Cl_3	=1328		
	6688		

Rational formula, $C_{36}\,H_{19}\,N\,O_{10} + HCl + PtCl_2$.

To separate narcogenin from its platinum compound, I intended to pursue the same plan as for the decomposition of the corresponding cotarnin salt. Complete decomposition, however, took place on ebullition in ammonia. The precipitate, separated by filtration from its dark mother-liquor and washed with distilled water, was dissolved in weak hydrochloric acid, and after boiling with animal charcoal, was again filtered and precipitated by potash. The base thus obtained was in the form of a white, extremely hygroscopic powder.

0·2145 grm. of this powder, dried at 100° C., gave carbonic acid 0·506, water=0·136.

	In 100 parts. Found.	Calculated.
Carbon	=64·33	65·62
Hydrogen	= 7·00	5·77

As the difference between the carbon and hydrogen found and calculated amounted to more than one per cent., I immediately prepared a platinum double salt directly from the base, to compare its analysis with that of the original platinum compound.

0·9255 grm. of this salt gave platinum 0·1455 = 15·73 platinum per cent.

The platinum per cent. in the original salt amounted to 18·10 grms.

0·3213 grm. burned with chromate of lead gave carbonic acid 0·5195, water 0·12.

	In 100 parts. Found.	Calculated.
Carbon	=44·09	40·38
Hydrogen	= 4·15	3·73

The two platinum salts have therefore a totally different constitution.

If an atomic weight of the base be calculated from 15·73, the platinum per cent. derived from the second platinum salt, the number obtained is 7846, from which, with the carbon and hydrogen found in the same platinum salt, the following formula is deduced, $C_{46}\,H_{25}\,N\,O_{14}$, $HCL + PtCl_2$.

	Calculated.	Found.
C_{46}	43·70	44·09
H_{26}	4·10	4·15
N		
O_{14}		
Pt	15·81	15·73
Cl_3		

This formula, however, expresses the composition of platinchloride of narcotine.

The same resemblance in composition is shown by a comparison of the per-centage of carbon of the base separated from the platinchloride of narcogenin and of that of narcotine. The hydrogen is a little too high, arising from the small quantity of substance used in the analysis, and from the extreme hygroscopic nature of the base in its precipitated state of powder. A repetition of its analysis after crystallization from alcohol gave 5·62 of hydrogen per cent.

	Base separated from platinchloride of narcogenin.	Narcotine.
Carbon	=64·33	64·61
Hydrogen	= 7·00 5·62	5·85

On crystallizing from alcohol, this base presents itself in the same form as narcotine, with which in its other physical properties it is identical. The peculiar metamorphosis which narcogenin had suffered on separation from its platinum double salt made it necessary to investigate the fluid from which the changed base had been separated. This ammoniacal liquid, which on filtration possessed a dark red colour, deposited on cooling a dirty whitish precipitate, from which it was decanted and then acted upon by a stream of sulphuretted hydrogen. On proceeding in the same way as that adopted for separating cotarnin from its platinum compound, a light greenish-coloured fluid was obtained, from which, on the addition of potash, crystals having the form of cotarnin were precipitated. These, after washing with distilled water, were redissolved in dilute hydrochloric acid and precipitated by bichloride of platinum. From this double salt, after combustion, the quantity of platinum per cent. obtained was 22·42. Platinchloride of cotarnin gave 22·88. The agreement of the physical properties as well as the amount of platinum per cent. prove the identity of the two substances. These analyses of the two bases derived from the decomposition of platinchloride of narcogenin, show that the latter cannot exist in an isolated form, but on separation from its double salt is converted into narcotine and cotarnin. The former remains on the filter, while the latter passes through

in solution in ammonia, accompanied by the double compound of platinum and ammonium, which has been reduced to the state of protochloride by the decomposition of water. The dirty looking precipitate which settles on the cooling of the fluid, is perhaps a small portion of the salt of Magnus mingled with foreign matter. The following table shows the decomposition which takes place:—

2 equiv. of narcogenin	$= C_{72} H_{38} N_2 O_{20}$
2 equiv. of oxygen from water decomposed in converting 2 equiv. of $Pt Cl_2$ to the state of PtCl . . .	$= O_2$
	$C_{72} H_{38} N_2 O_{22}$

Produce.

1 equiv. of narcotine	$= C_{46} H_{25} N O_{14}$
1 equiv. of cotarnin	$= C_{25} H_{13} N O_6$
1 equiv. of carbonic acid	$= C O_2$
	$C_{72} H_{38} N_2 O_{22}$

A comparison of the formula of narcotine deduced from direct analysis, and of its products of decomposition, show a very simple relation.

By the employment of a large excess of bichloride of platinum, the products obtained are cotarnin, opianic acid, carbonic acid and water. Along with these also is found the almost constantly accompanying hemipinic acid, derived from the further oxidation of the opianic.

1 equiv. of narcotine . . .	$= C_{46} H_{25} N O_{14}$
+ 7 equiv. of oxygen . . .	$= O_7$
	$C_{46} H_{25} N O_{21}$

Produce.

1 equiv. of cotarnin . . .	$= C_{25} H_{13} N O_6$
1 equiv. of opianic acid . .	$= C_{20} H_9 O_{10}$
1 equiv. of carbonic acid .	$= C O_2$
3 equiv. of water	$= H_3 O_3$
	$C_{46} H_{25} N O_{21}$

The further oxidation of opianic acid gives from

1 equiv. of anhydrous opianic acid .	$= C_{20} H_8 O_9$
+ 1 equiv. of oxygen	$= O$
2 equiv. of anhydrous hemipinic acid	$= C_{20} H_8 O_{10}$

To prove the disengagement of carbonic acid, the oxidation by bichloride of platinum was conducted in an atmosphere of hydrogen. The amount obtained, though quite conclusive of the fact of its evolution, was not large, being according to theory only one equivalent in 46.

If only a very small excess of bichloride of platinum is employed, the decomposition of narcotine does not proceed so far. The principal product is now platinchloride of narcogenin, accompanied by smaller quantities of opianic and hemipinic acid. Traces of platinchloride of cotarnin are also observed.

2 equiv. of narcotine . .	$= C_{92} H_{50} N_2 O_{28}$
+5 equiv. of oxygen . . .	$= \underline{\qquad\qquad O_5}$
	$C_{92} H_{50} N_2 O_{33}$

Produce.

2 equiv. of narcogenin . .	$= C_{72} H_{38} N_2 O_{20}$
1 equiv. of opianic acid .	$= C_{20} H_9 O_{10}$
3 equiv. of water . . .	$= \underline{H_3 \quad O_3}$
	$C_{92} H_{50} N_2 O_{33}$

The hemipinic acid is, as stated before, a product of the decomposition of opianic acid.

The same precaution of conducting the oxidation in an atmosphere of hydrogen was also here observed. The lime-water became only very slightly opalescent after continuing the ebullition for a considerable time. The evolution of carbonic acid at this stage may be owing to the small quantity of cotarnin accompanying in most cases the formation of narcogenin; but more probably to the decomposition of the latter, which by further oxidation is converted into opianic or hemipinic acid, with disengagement of carbonic acid. Of the decomposition of platinchloride of narcogenin in this manner I convinced myself by direct experiment. A portion of this salt boiled in a large excess of bichloride of platinum with the precaution already mentioned, gave off carbonic acid freely, and was changed into the platinum salt of cotarnin. The mother-liquor separated from the latter gave crystals of opianic or hemipinic acid, according to the duration of the boiling.

The following table exhibits these changes:—

2 equiv. of narcogenin	$= C_{72} H_{38} N_2 O_{20}$
+9 equiv. of oxygen .	$= \underline{\qquad\qquad O_9}$
	$C_{72} H_{38} N_2 O_{29}$

Produce.

2 equiv. of cotarnin .	$= C_{50} H_{26} N_2 O_{12}$
1 equiv. of opianic acid	$= C_{20} H_9 O_{10}$
2 equiv. of carbonic acid	$= C_2 O_4$
3 equiv. of water . .	$= \underline{H_3 \quad O_3}$
	$C_{72} H_{38} N_2 O_{29}$

It is probable that bichloride of platinum has the same oxidizing action on many of the other organic bases. This cir-

cumstance may account for the difference of their atomic weights when calculated from their platinum double salts. Upon morphia its action is even more marked than upon narcotine. On boiling the former in an excess of the bichloride, the liquid becomes immediately of a very dark colour, apparently black, by reflected light. There is at the same time formed a platinum salt of another base, and a dark brown granular looking acid, which is insoluble in water, alcohol and æther, forms soluble salts with potash and ammonia, and an insoluble salt with silver. This subject has not yet been examined by me, but I intend to return to it, and hope before long to communicate the results of its further investigation.

CXIV. *On the Inorganic Constituents of Plants.* *By* Drs. H. Will *and* R. Fresenius.

SINCE the true value and importance of inorganic constituents for the existence of plants has been pointed out and established by Professor Liebig, it has become an object of high interest in vegetable physiology and agriculture, to possess an extended series of trustworthy analyses of the ashes of different plants, and of different parts of plants, conducted with reference to the points to which the Professor has directed attention in his work, "Organic Chemistry in its applications to Agriculture and Physiology." We say trustworthy, and thus specially directed analyses, since in those already at command the requisite conditions are but partially supplied.

To the exemplary labours of De Saussure concerning vegetation, is due the undisputed merit of having first incited to a knowledge of the importance of the inorganic constituents of plants; he established the fact by means of numerous analyses of vegetable ashes. The methods of chemical analysis, and especially of the quantitative estimation of the more important constituents of vegetable ashes (phosphoric acid for example), were not however at that time such as to render the results of De Saussure available for the determination of the functions fulfilled in plants by inorganic acids and bases.

Berthier* has also made a considerable number of analyses of the ashes of various woods; his only object however was to ascertain, if possible, what effects the ashes of the wood used as fuel in metallurgy would have upon those processes.

Berthier found by a comparison of his carefully obtained analytical results, that the nature of the ash depended to some extent upon the properties of soil; he observed that the composition of the ashes of the same kind of wood grown on different

* *Ann. de Chimie et de Phys.* xxxii. p. 240.

soils, differed considerably; he showed also that the ashes of different kinds of plants grown upon the same soil were dissimilar, and that plants which are identical or allied in kind, when grown upon the same soil, yield ashes, the compositions of which are also either allied or identical. Finally, Wiegmann and Polstorff*, by ascertaining the quantity of ashes of plants which have vegetated in sand and in artificial mould, have clearly shown that the increase of plants, their growth, and full development are inseparably connected with the organic materials contained in the earth, and that plants will not perfect their seeds if the earth is deficient in phosphates, &c.

All recorded observations clearly show that plants take up indiscriminately the soluble mineral constituents presented to them by the soil; and the results of ash-analyses as distinctly prove, that for the purpose of assimilation by their different parts and organs, they make a selection from those constituents; that the organism of vegetables, like that of animals, takes up and retains those substances which it requires.

It follows from what has been said, that in the analysis of ashes, a number of substances will be found which have not entered into the composition of any organ of the plant, substances which have been dissolved by the juices of the plant; and, since we have no means of safely separating them for the purposes of analysis, they will remain after the ignition mixed with the assimilable and assimilated mineral constituents of the plant.

Nature has provided in the seeds of plants, as in the eggs and milk of animals, all the substances which are necessary for the development of the young individual, so long as it is itself incapable of seeking sustenance externally. In the ashes of seeds we shall find therefore treasured up, and almost pure, the indispensable mineral food of the plants.

The examinations hitherto made of the ashes of seeds indicate that those of the *Cerealia*, the *Leguminosæ*, the *Cruciferæ*, and among arboreous plants, the *Coniferæ*, consist almost entirely of the alkaline and earthy phosphates. They do not effervesce with acids, they contain however variable quantities of silica and sulphates, but chlorides are either entirely wanting, or merely traces of them exist. The ashes of the seeds of the oak, of the chestnut and of the beech, and probably of many other trees, effervesce strongly with acids; besides phosphates they contain a considerable quantity of carbonates, which have resulted from the salts of vegetable acids contained in the seeds. The proportion of chlorides, sulphates

* *Ueber die unorgan. Bestandtheile der Pflanzen; gekrönte Preisschrift.* Braunschweig, 1842.

and silica to the other constituents, is also in these ashes but small.

We conclude from these facts, that the salts of phosphoric acid are indispensable mineral constituents of the Cerealia, &c., and that the oak and the chestnut, &c. require, besides these, alkalies not united with mineral acids.

It would be very difficult at present accurately to distinguish the so-called essential and non-essential constituents of ashes. A plant requires for its different parts, and at different periods of its growth, a supply of mineral constituents, varying both in quantity and in quality. There is no ash-constituent which we can as yet decide to be entirely unessential. We can however distinguish those which have been assimilated by the plant and have formed a part of it from those which are within the plant, without having been assimilated by it, but await, as it were, their approximation in its future development and maturation. Among the latter we may class the alkaline chlorides and the sulphates, which are always present in vegetable ashes; they exist in the form of soluble compounds in the juices of every plant, and are doubtless indispensable to it, as yielding some of its elements; we have however as yet no reason for supposing that they themselves become constituents of the organs of the plant. According to Guibourt (*Journ. de Pharm.* xxvi. p. 264), the ashes of juicy saline plants contain only 17 per cent. of chlorides to 69 per cent. of carbonates. It would seem highly probable that the bases of salts of vegetable acids are derived from chlorides; the chlorides in this case suffer a decomposition, in which the electro-negative element plays but a subordinate part. These chlorides, which seem so necessary for saline plants, may probably be replaced by other compounds of the same basyles, provided they be not injurious to the plants, and that they be equally soluble with the chlorides, and consequently existing as largely in the juices of the plant.

We have further reason for supposing these constituents to be unessential, from the fact that their quantities from the same kind of plants are variable, without there being evidence that they are replaced by any other body. The quantity of sulphates found in an ash will, however, to some extent, be dependent on the management of the preparation of the ash. If a strong heat, with free access of air, be permitted, part if not all of the sulphur contained in nitrogenized vegetable substances will be converted into sulphuric acid during the ignition. On the other hand, however, if the ash has not been heated sufficiently long with free access of air, the addition of an acid to a portion of it will cause the evolution of a not inconsider-

able quantity of sulphuretted hydrogen, the source of which has been the deoxidized sulphates. In such a case, if it be wished to make a quantitative analysis of the ash, it must be heated with free access of air until the sulphurets are fully oxidated.

The carbonic acid, and the charcoal found in the ashes of most vegetable substances (with the exception of some seeds), are always to be viewed as accidental constituents, having their origin in the operation of combustion; their quantity also is dependent both upon the quantity and quality of the bases present, and upon the degree of heat which has been employed.

We now submit to view a list of the *inorganic* compounds or bodies which have hitherto been found in the normal ashes of vegetables. They are as follow:—

Bases.	Acids or bodies which replace them.
Potash.	Silicic acid.
Soda.	Phosphoric acid.
Lime.	Sulphuric acid.
Magnesia.	Carbonic acid.
Peroxide of iron.	Chlorine.
Oxide of manganese.	Iodine.
Alumina.?	Bromine.
	Fluorine*.

With the exception of iodine, bromine, fluorine and oxide of manganese, the acids and bases enumerated above are found in almost all vegetable ashes. Several chemists have stated that alumina also is found in the ashes of plants. Berthier, on the other hand, did not find a trace of it in the ashes which

* It has long been known that marine plants, and consequently their ashes also, contain iodine and bromine. In some the quantity of iodine is so considerable, that they are had recourse to in commerce for the production of that element, as in Scotland, for example. The existence of fluorine in some vegetable ashes, although extremely probable, has not been proved until recently. Careful experiments, conducted under my own superintendence, by Messrs. James, Müller and Blake severally, have shown that the ashes of French barley, grown in Switzerland, contain very distinct traces of it; both straw and grain were employed. The presence of silica in considerable quantity renders the detection of fluorine very difficult. The process followed was that of H. Rose, which consists in fusing the ash with carbonated alkali, dissolving in water, neutralizing with hydrochloric acid, in a platinum capsule, adding ammonia in excess, after expelling the carbonic acid by evaporation, and precipitating the filtered solution by means of chloride of calcium. In this experiment not less than 10 to 12 grammes of ash should be employed. Fluorine occurs in the teeth and bones of animals, having been derived by them from vegetable food; it will doubtless therefore exist still more abundantly in the ashes of plants: it almost constantly accompanies phosphoric acid, and must therefore be almost as generally diffused on the earth's surface as that acid itself, which is so indispensable both for the vegetable and animal kingdoms.—H. Will.

he examined, and we have been unable to detect it in all carefully prepared ashes. De Saussure states that the ashes of the bilberry, the pine and the rose-laurel, contain respectively 17·5, 14·8 and 28·8 per cent. of alumina; it is evident however that he has mistaken the earthy phosphates for that substance, and when in subsequent analyses he determined the phosphates, he found no alumina, or merely a trace of it. The behaviour of alumina with solvents sufficiently proves that it cannot be taken up by plants. Pure alumina is equally insoluble in solutions of phosphoric and of carbonic acid; and though we find in almost all vegetable ashes phosphate of the peroxide of iron, which is so nearly allied to alumina in insolubility, it has probably been taken up by the plant as phosphate of the protoxide, which is soluble in a solution of carbonic acid. If the aluminous compounds, which are so abundant in the soil, were soluble, we should find them in all vegetable ashes; and even were the presence of alumina demonstrated in particular cases, we have sufficient reason for supposing that it, as well as the sand, which is frequently met with in the analyses of ashes, has been derived from dust, which has not been removed from the plant with sufficient care previously to the preparation of the ash.

Oxide of copper has also been found occasionally in vegetable ashes; Meissner and Saczeau observed it in those of the Cerealia. In some parts of Germany the seeds of the Cerealia are steeped in a solution of sulphate of copper before being sown, with a view of preventing the destruction of the crop by blight: and when oxide of copper is found in vegetable ashes, it may be attributed either to such treatment, or to the presence of cupreous minerals in the soil; it is always however to be looked upon as unessential or accidental, and not as a necessary constituent of the ashes of the plant.

The relative proportions of the constituents of vegetable ashes vary so much, according to the nature of the plant, or the part of the plant (and also according to the properties of the soil), that it has been attempted to classify plants by reference to the predominant constituent of their ashes. Such a classification will only be attainable when we can, with respect to a large number of analyses, ensure the necessary accuracy: for our immediate purpose, however, that of arranging a method of quantitative ash-analysis, the ashes of vegetables can be generally classed according to the prevalence of some of their constituents.

All vegetable ashes can be arranged according to their composition in the three following groups:—

(a.) *Ashes rich in Alkaline and earthy Carbonates.*—To this

group belong the ashes of woods, herbaceous plants and lichens, inasmuch as these abound in salts of organic acids.

(b.) *Ashes rich in Alkaline and earthy Phosphates.*—Almost all seeds yield ashes belonging to this division.

(c.) *Acids rich in Silica.*—The stems of the Grasses, the Equisetaceæ, &c., yield ashes of this kind.

It will be seen that this classification cannot be strict, and that besides the instances already known, many others will occur of members of the different classes assimilating. The ashes of the mistletoe (*Viscum album*), for example, form a link between the first and second groups, inasmuch as they contain considerable quantities both of carbonates and of phosphates; the same may be said of those of the seeds of the oak (*Quercus robur*) and of the chestnut (*Fagus castanea*). Again, the ashes of some seeds, as millet (*Millium sativum*), oats (*Avena sativa*), barley (*Hordeum vulgare*), contain so much silica that they might with equal propriety be placed in the third as in the second group.

The division of plants into potash, lime and silica plants is quite inadmissible, since it would be inconsistent with the beautiful law of substitution established by Professor Liebig. According to this law, the predominance of the one or the other of the above-named bases in the ashes of a plant depends upon the quantities of each existing in the soil. Tobacco would generally be considered as belonging to the lime group; the result of recent analyses, of great interest in reference to the law mentioned above, prove however that tobacco would equally belong to the potash group if grown upon a soil in which that base abounded.

We now proceed to describe a method of quantitative ash-analysis which, as yet, we have found to be the simplest, and therefore most to be depended upon. The details of the process comprise but little that is new to science, whilst a method, more or less similar, might easily have been arranged by any experienced chemist. We are nevertheless of opinion that circumstances justify its ample consideration. The subject is as yet but partially investigated, and there are doubtless chemists appreciating its importance, and desirous of entering upon the inquiry, to whom it will be a desideratum to be possessed of a method, into the correctness of which they need not themselves laboriously examine.

Method of Quantitative Ash-analysis.

I. *Preparation of the Ash.*—It is evident that the removal of all foreign matter from the vegetable substances selected is of the greatest importance: whether seeds, herbs or roots,

they should be carefully examined and freed from adherent dirt before being burned. They must not be washed, however, since in that case some of the soluble salts would be extracted; for the same reason, plants which have been exposed in a withered or dead state, to rain or moist weather, should not be employed. Plants in a healthy and natural condition should always be selected, unless the object in view be the study of disease and its causes.

The information sought by means of ash-analysis, may have reference to the quantity and quality of the inorganic matter contained in a particular kind of plant, or part of a plant; or it may be desired by its aid to judge of the properties of the soil, as regards the presence in it of alkalies, alkaline earths and phosphates. If the latter be the object, a quantitative examination of the ashes of all the plants grown upon the soil will frequently suffice. A knowledge being once attained of the composition of the ashes, both of the cultivated plants and of the weeds, we shall be enabled to decide respecting the composition of the soil, and its suitableness for the production of each particular plant.

Woods, herbs and roots, after being thoroughly dried, should be burned upon a clean iron plate; but for leaves, fruits and seeds, it is more convenient to employ a hessian crucible, heated by means of burning charcoal, in which it is placed somewhat obliquely. The ash is occasionally very easily burned white, but some seeds require a more elevated temperature, to get rid of the charcoal which is intimately mixed with the phosphates; care should always be taken, however, to avoid heating so strongly as would cause the fusion or softening of the alkaline salts, should they abound, or it will be quite impossible to burn the charcoal, which in that case becomes inclosed in the mass. It has properly been observed by De Saussure, that the ashes are whitest when the access of air has not been impeded by stirring or shaking them together.

The ash thus prepared should, if necessary, be further heated to low redness in an open platinum capsule, over a spirit-lamp, with constant stirring; afterwards, and whilst still warm, it should be rubbed to a very fine powder, intimately mixed, and put into a well-closed bottle.

It is now determined, by means of a qualitative analysis, to which of the three groups the ash belongs. Its solubility in concentrated hydrochloric acid is first ascertained: this is in most cases complete, unless the ash be obtained from the stems of the grasses, which abound in silicic acid.

After the separation of the silica, the acid solution is treated

with acetate of ammonia, or it may be neutralized by means of caustic ammonia, free acetic acid being then added; in most cases a yellowish-white gelatinous precipitate is formed, which consists of phosphate of the peroxide of iron. This precipitate is collected upon a filter, and ammonia is added in excess to the clear solution, by which a fresh precipitation will generally be occasioned. If a red precipitate be formed, it is peroxide of iron; if, after standing some time excluded from the air, no precipitation takes place, we conclude that the ash contains no phosphate besides the one previously separated; but if a white precipitate be formed (phosphate of lime and phosphate of magnesia), it is known that there is more phosphoric acid present than is required to combine with the peroxide of iron. Nothing further is necessary for the completion of the *qualitative* analysis, but to test for fluorine and oxide of manganese, and, in the case of marine plants, for iodine and bromine; unless, indeed, it happen that the experimenter have reason to suspect the presence of other substances in the ash.

For the determination of the chlorine (iodine and bromine) and of the carbonic acid, separate portions of ash are always employed, as also for that of the alkalies, in ashes belonging to the third group. All the other constituents are determined in one quantity of ash, so that the silica has only to be separated once.

A. *Analysis of Ashes rich in Carbonates and Phosphates.*

1. *Determination of the Silica of the Charcoal and of the Sand.*—About 4 grammes of the ash, which has been found to be soluble in hydrochloric acid, is treated with the concentrated acid in a matrass, held obliquely, so as to avoid the loss of fluid during the evolution of carbonic acid; gentle heat is then applied, until it is evident that everything is dissolved, excepting the carbonaceous and sandy particles. The whole is now carefully removed into a porcelain basin, evaporated to dryness over a water-bath, and then heated somewhat more strongly, as is usual in separating silica. The mass when cold is moistened with strong hydrochloric acid, is digested for half an hour with a sufficient quantity of water, and is boiled, after which the acid liquid is poured upon a stout filter which has been previously dried at 100° C. and weighed.

The silica will remain upon the filter, and if the ash was not perfectly white and pure, some sand and charcoal also. The filter is washed and dried, and the substance carefully removed from it into a platinum crucible without injury to the paper. This is easily effected if the matters be perfectly dry, the paper in most cases only retaining so much as to be

slightly coloured by the charcoal. The powder is now boiled for half an hour with pure potash ley (free from silica), by which the whole of the silica will be gradually dissolved, leaving the sand and the charcoal unacted upon. The insoluble matter is again collected on the same filter, washed, and dried at 100°C. until it no longer loses weight. The increase upon the weight of the dried filter is estimated as charcoal and sand.

The filtered solution, after the addition of hydrochloric acid in excess, evaporation to dryness, and treatment in the usual way, gives the quantity of silica.

The acid solution, originally filtered from the silica, sand and charcoal, after being well mixed, is divided into three, or more conveniently into four equal portions, one being reserved in case of misfortune with either of the other quantities. The division is best accomplished by means of an accurately graduated tube: the whole of the fluid is collected into the tube, the entire measure then representing the weight of ash experimented upon. The solution is now divided into three or four equal or known portions, the volume of each is noted, and they are distinguished by the letters *a*, *b*, *c* and *d*.

In (*a*) the peroxide of iron, oxide of manganese, and the alkaline earths are estimated.

In (*b*) the alkalies.

In (*c*) the phosphoric and sulphuric acids.

2. *Estimation of the Peroxide of Iron and of the Alkaline Earths.*—To the solution (*a*) ammonia is added until the precipitate which is thereby produced no longer entirely redissolves; acetate of ammonia is next added, and sufficient acetic acid to render the solution strongly acid. From the form and appearance of the precipitate it can easily be judged whether it still contains phosphate of lime; if this be the case, more acetic acid must be added. The yellowish-white precipitate which remains consists of phosphate of the peroxide of iron, $2Fe_2O_3 + 3PO_3$. Its separation from the fluid is assisted by gently heating it, it is then well washed upon a filter with hot water, ignited and weighed *.

* We have submitted to careful analysis the white, or rather greenish-yellow precipitate, formed by mixing solutions of the common phosphate of soda and a persalt of iron. The formula of this compound, when dried without heat over sulphuric acid, is $2Fe_2O_3 + 3PO_5 + 13Aq$. Of these 13 equivalents of water 6 go off at 100° C., 4 more at from 300° to 400°, but the remaining 3 are only expelled by strong ignition. The rational formula is therefore $3PO_5, 2Fe_2O_3, 3HO + 4HO + 6Aq$. The numbers obtained by analysis were as follow:—

I. 1·8087 grm. of the substance dried over sulphuric acid lost at 100° C. 0·199 water = 1·100 per cent., and 0·131 more = 7·24 per cent. at 300° to 400°.

II. 1·4787 of the salt dried at 300° to 400° C. lost by ignition in one ex-

To the filtered solution neutral oxalate of ammonia is added as long as a precipitate is formed, and the quantity of lime is determined in the usual manner. When it has been shown by quantitative analysis, that besides phosphate of iron, the ash contains peroxide of iron or oxide of manganese (in which cases the presence of earthy phosphates is very rarely detected), the solution, previously to the separation of the lime, should be supersaturated with ammonia and precipitated by means of sulphuret of ammonium; the two oxides being afterwards separated according to the known methods.

If the ash under examination contained earthy phosphates, the solution filtered from the oxalate of lime will contain free acetic acid; if otherwise, ammonia will be free; it is next somewhat concentrated, rendered ammoniacal, treated with a solution of phosphate of soda, and separated from the precipitate, which is estimated as phosphate of magnesia.

3. *Estimation of the Alkalies.*—The solution (*b*) is treated with baryta water until it gives an alkaline reaction, it is then gently heated and filtered. By this means we get rid of all the sulphuric acid, phosphoric acid and peroxide of iron, as well as the magnesia and most of the lime. The precipitate is washed upon a filter as long as the liquid renders turbid a solution of nitrate of silver; the solution is next warmed, treated with caustic ammonia and carbonate of ammonia, and allowed to stand until the precipitate becomes heavy and granular. The whole is now filtered, and the solid matter is washed, after which the solution is evaporated to dryness, and the residue heated to redness in a platinum capsule to expel the ammoniacal salts. What remains consists of the chloride of potassium or sodium, or more generally of a mixture of the two. The weight being noted, a little water is added, which mostly leaves undissolved a trace of magnesia; this is collected on a filter, its quantity is subtracted from that

periment 7·13 per cent., and in second 6·62 per cent. water; the mean is 6·87 per cent. = 5·61 per cent. of the salt not dried at an elevated temperature.

III. 0·409 of the salt dried at 300° (= 0·5015 dried over sulphuric acid) yielded 0·158 peroxide of iron = 31·5 per cent.

The composition of the salt is therefore—

		In 100 parts.	
		Calculated.	Found.
$2Fe_2O_3$ . . .	1957	32·09	31·50
$3PO_5$	2678	43·92	
3HO	337	5·54	5·61
4HO	450	7·38	7·24
6Aq.	675	11·07	11·00
		100·00	

of the supposed alkaline chlorides and added to that of the magnesia as previously ascertained. The quantity of potash is determined by means of chloride of platinum in the usual way; and that of the soda is calculated from that of the chloride of sodium, indicated by deducting the weight of the chloride of potassium from that of the mixed alkaline chlorides.

4. *Estimation of the Sulphuric and Phosphoric Acids.*—From the acidulous solution (*c*), the sulphuric acid is first separated by means of chloride of barium. The filtered liquid is nearly neutralized with ammonia, acetate of ammonia is added, and then a solution of perchloride of iron, until the liquid begins to turn red, owing to the formation of acetate of iron. Care must here be taken that sufficient acetate of ammonia be added to convert the whole of the chlorine of the perchloride into sal-ammoniac. The solution is now boiled until it is colourless, all the iron being then precipitated. The precipitate, after being washed with hot water, consists of phosphates of iron and a quantity of basic acetate of iron. It is dried, ignited in a platinum crucible, treated with a few drops of nitric acid, re-ignited and weighed. It is next digested with concentrated hydrochloric acid, which speedily dissolves it. The solution is diluted with hot water mixed with tartaric acid, and ammonia is added until the yellowish-white precipitate which is at first formed disappears. A clear solution, but of a dingy green colour, is thus obtained, from which the iron is precipitated by means of sulphuret of ammonia. The precipitate and supernatant fluid are digested together in a warm place until the latter loses its green tinge and is of a clear yellow colour, resembling that of the sulphuret of ammonia. It is now rapidly filtered, access of air being excluded, and the precipitate is washed with hot water containing a little sulphuret of ammonia, until a drop of the filtered liquid, dried upon a platinum spatula and ignited, no longer indicates an acid reaction. The sulphuret of iron is dissolved from the filter by means of hot and dilute hydrochloric acid, the solution is boiled, treated with a few drops of nitric acid to peroxidize the iron, and ammonia is then added in excess. The precipitate is pure peroxide of iron, whose weight, deducted from that of the basic phosphate, gives the quantity of phosphoric acid. It is essential that the perchloride of iron used in this experiment be quite free from sulphuric acid.

5. *Estimation of the Chlorine.*—A fresh portion of ash (about 1 gramme) is weighed out, exhausted by means of hot water slightly acidulated with nitric acid, and the solution is precipitated with nitrate of silver. If the ash contain appreciable quantities of iodine or bromine, these bodies will be found in

the precipitated silver-salt; for their quantitative estimation, however, a larger portion of ash must be employed.

6. *Estimation of the Carbonic Acid.*—The quantity of carbonic acid is represented by the loss sustained on treatment of a known weight of ash with an acid; and we have elsewhere described the most convenient method and apparatus for the experiment.

B. *Analysis of Ashes abounding in Silica.*

Ashes of this kind, as we have already observed, are generally only partially soluble in acids; their alkalies must therefore be determined in a separate portion of ash. The chlorine and carbonic acid are determined in the same manner as when the ash is entirely soluble in acids. The quantity of chlorine found in ashes of this class is however probably always somewhat less than it should be, since the alkaline chlorides, when ignited with silica and carbon, undergo a partial decomposition.

1. *Estimation of the Silica, &c.*—Pure potash or soda ley is poured upon about 4 grammes of the ash and evaporated to dryness in a platinum or silver dish. The silicic acid compounds are by this treatment dissolved, leaving the sand unaffected. The heat should not be so great as to fuse the mass, or some of the charcoal will be oxidated at the expense of the water of the hydrated alkali. Dilute hydrochloric acid is poured upon the mass, the whole evaporated, and the silica, charcoal, &c. determined in the manner already described. The acidulous solution filtered from the insoluble matter is divided into two parts; one is employed for the determination of the sulphuric and phosphoric acids, and the other for that of the peroxide of iron and the alkaline earths, by the methods detailed above.

2. *Estimation of the Alkalies.*—A second portion of ash (say 3 grammes) is ignited in a crucible of platinum or silver with four times its weight of hydrated barytes, the acid solution which remains after separating the silica, &c. is precipitated successively with barytes water, and carbonate of ammonia, the alkalies being then obtained in the state of chlorides.

C. *Determination of the Quantity of Ash.*

It is often important, even indispensable, to ascertain the entire quantity of inorganic constituents contained in a plant or part of a plant. A certain quantity of fixed matter is annually removed from cultivated land in the crop, and it is a desideratum to have a scale for the reparation of this loss by means of manures. The chemist who is engaged with ash-analysis should therefore acquire information as to the quantity which will be

taken from a given surface by the crop. Rational agriculturists and woodreeves are always in possession of details of this kind, which are generally of sufficient accuracy for the ends to be answered by them.

The vegetable substance under examination should be dried over a water-bath at 100° C. until it no longer loses weight; if however any of its constituents be volatile, the drying is best conducted over sulphuric acid, without the application of heat. The quantity of substance to be burned to ash will depend upon the quantity of fixed matter it contains. Of herbs and seeds, which are rich in inorganic constituents, 2 to 3 grammes will be sufficient; of woods, however, which frequently contain only 0·2 per cent. of fixed matter, ten or more times that quantity must be taken. The combustion succeeds best in a thin platinum crucible; it is at first covered and heated only gently, but afterwards the lid is removed and a stronger heat employed until the whole of the charcoal is consumed. The ashes of seeds which do not effervesce with acids may be moistened with nitric acid and re-ignited, when they will very speedily be turned white.

We now submit a number of ash-analyses which were conducted according to the methods we have described. The first are those of ten kinds of tobacco, which were sent to Professor Liebig for the purpose by the director of the Imperial Austrian tobacco manufactory in Vienna. All these plants were cultivated in Hungary, upon land which had never been manured, and upon which the same plant had been grown for a considerable length of time.

The specimens 1, 2 and 3 were from the Debreczyner, No. 4 from the Banat, and Nos. 5 to 10 inclusive from the Fünfkirchner district. With the exception of Nos. 7, 8, 9 and 10, the leaves reached us in a sound and perfectly healthy state, still partially retaining their green colour. Differences were however clearly indicated by the varying size and greater or less luxuriance of the specimens.

In addition to the above we analysed the ashes of the grain of red and of white wheat (*Triticum vulgare*), of the seed and of the straw of rye (*Secale Cereale*), of peas (*Pisum sativum*), of the wood of the apple-tree (*Pyrus malus*), of the mistletoe (*Viscum album*) from the same tree, and of lichens (*Parmelia prunastri*, *fraxinea*, *parietina*, *furfuracea*): all were grown in the neighbourhood of Giessen.

Tabulated Results of the Analyses of the Ashes of Tobacco.

(A.) *Actual results of the analyses of* 100 *parts of Ash.*

	Debreczyner.			Banat.	Fünfkirchner.					
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
					1840.	1841.	Dried at the temperature of a room.	Powder of leaves. 1841.	Powder of stalk.	Powder of leaves. 1839.
Potash	23·33	22·90	22·63	14·48	5·77	13·62	6·28	6·01	7·35	6·55
Soda	1·81	.....	.....	.....	.....	0·19				
Lime	22·19	18 51	25·29	22·16	30·08	30·99	31·98	31·74	27·09	27·44
Magnesia	5·79	5·79	5·93	12·51	9·80	7·71	9·46	10·01	10·31	7·46
Chloride of sodium	0·73	4·44	7·59	9·07	2·27	2·46	2·99	2·06	4·38	1·51
Chloride of potassium	.....	.....	3·98	3·12	6·00	.....	2·88	2·10	2·05	1·74
Phosphate of peroxide of iron	7·04	4·50	5·19	5·41	4·27	3·02	3·37	4·32	5·19	3·69
Phosphate of lime	.....	.....	.....	.....	.....	4·16				
Sulphate of lime	5·16	4·50	5·22	8·04	5·60	3·92	4·34	3·94	6·46	3·00
Silica	14·16	13·73	5·35	4·75	6·54	3·58	3·59	4·03	5·72	7·04
Carbonic acid	10·45	9·11	14·78	15·90	15·09	21·95	22·69	17·08	17·30	17·49
Charcoal and sand	10·31	13·50	4·73	6·46	13·72	8·04	11·62	19·36	13·80	23·75
	100·97	97·28	100·69	101·90	99·14	99·64	99·20	100·65	99·74	99·70

(B.) *Product of* 100 *parts of Ash, after deducting the carbonic acid, the charcoal and the sand.*

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Potash	29·08	30·67	27·88	18·20	8·20	19·55	9·68	9·36	10·37	11·21
Soda	2·26	.....	.....	.....	.....	0·27				
Lime	27·67	24·79	31·16	27·86	42·77	44·49	49·28	49·44	39·53	47·03
Magnesia	7·22	8·57	7·31	15·73	13 93	11·07	14·58	15·59	15·04	12·77
Chloride of sodium	0·91	5·95	9·34	11·41	3·22	3·54	4·61	3·20	6·39	2·58
Chloride of potassium	.....	.....	4·90	3·92	8·53	.....	4·44	3·27	2·99	2·97
Phosphate of peroxide of iron	8·78	6·03	6·39	6·80	6·07	4·34	5·19	6·72	7·56	6·30
Phosphate of lime	.....	.....	.....	.....	.....	5·97				
Sulphate of lime	6·43	5·60	6·43	10·11	7·96	5·63	6·68	6·14	9·42	5·11
Silica	17·65	18·39	6·59	5·97	9·32	5·14	5·54	6·28	8·34	12·03
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Oxygen in the bases united to organic acids	16·06	15·47	16·31	16·99	18·78	20·15	21·09	21·50	18·75	20·05
Per-centage of ashes obtained from the dry leaves	18·9	22·2	24·5	19·8	23·0	21·08	23·28	23·28	22·83	27·36

(A.) *Actual Results of the analyses of* 100 *parts of the ashes of*

	Wheat.		Rye.		Peas.	Apple-tree.		
	Red. Grains.	White. Grains.	Grain.	Straw.		Wood.	Mistle-toe.	Lichen.
Potash	20·80	30·17	31·89	17·03	39·25	13·67	35·32	10·07
Soda	15·01	.. ...	4·33	.. ...	3·96	0·32	.....	
Lime	1·83	2·76	2·84	8·98	5·87	45·19	19·40	10·33
Magnesia	9·12	12·08	9·86	2·39	6·41	5·30	9·59	5·33
Peroxide of iron	1·29	0·28	0·80	1·35	1·04			
Phosphate of peroxide of iron	.....	.....	.....	.....	.....	1·71	1·83	14·56
Phosphoric acid	46·91	43·89	46·03	3·80	34·23	2·95	16·56	
Chloride of sodium	.....	.....	trace.	0·56	3·69	0·32	1·02	
Chloride of potassium	.....	.....	.....	0·25				
Sulphuric acid	.....	.....	1·42	0·81	4·89	0·66	1·41	
Silica	0·15	.....	0·17	63·89	.....	0·93	1·62	
Carbonic acid	.....	.....	.....	.....	.....	24·18	13·09	4·64
Charcoal and sand	4·89	9·03	2·66	0·94	1·38	2·03	0·54	49·73
	100·00	98·21	100·00	100·00	100·72	97·26	100·38	94·66*

* The remaining constituents were not estimated.

(B.) *Per-centage composition after deducting the carbonic acid, the charcoal and the sand.*

	Wheat.		Rye.		Peas.	Apple-tree.		
	Red. Grains.	White. Grains.	Grain.	Straw.		Wood.	Mistle-toe.	Lichen.
Potash	21·87	33·84	32·76	17·19	39·51	19·24	40·71	
Soda	15·75	.....	4·45	.....	3·98	0·45	.....	
Lime	1·93	3·09	2·92	9·06	5·91	63·60	22·37	
Magnesia	9·60	13·54	10·13	2·41	6·43	7·46	11·06	
Peroxide of iron	1·36	0·31	0·82	1·36	1·05			
Phosphate of peroxide of iron	.....	.....	.....	.....	.....	2·41	2·11	
Phosphoric acid	49·32	49·21	47·29	3·82	34·50	4·15	19·09	
Chloride of sodium	.....	.....	.....	0·57	3·71	0·45	1·17	
Chloride of potassium	.....	.....	.....	0·26				
Sulphuric acid	0·17	.....	1·46	0·83	4·91	0·93	1·62	
Silica	.....	.....	0·17	64·50	.....	1·31	1·87	
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	
Quantity of oxygen in the bases of the phosphates	12·35	11·92	11·97	.....	11·18			

On comparing these analyses of tobacco-ash, it is at once seen that plants of the same kind, grown upon the same soil, yield ashes, the composition of which differs but little. This is very evident with respect to those of the Debreczyner leaves (1, 2 and 3). The proportion of bases combined with organic acids is, so far as their oxygen is concerned, very nearly the same in each case. The quantity of lime in the ashes of the Banat leaves is almost the same as in those of the Debreczyner leaves, whilst the quantity of potash in the former is scarcely two-thirds as great as in the latter; the quantity of magnesia, however, the equivalent of which is so small, is nearly doubled. The ashes of the Fünfkirchner leaves exhibit a still wider difference; in four instances the quantity of potash is scarcely one-third of that in the Debreczyner leaves; in place of this potash, however, we find an increase in the quantity of lime, amounting to nearly 50 per cent. Again, the quantity of magnesia is the same as in the ashes of the Banat leaves, whilst the lime in the latter only amounted to 27 per cent.

It is evident that these differences depend entirely upon the variable quantities of the several bases contained in the soils. In these differences we recognise moreover a beautiful confirmation of the law of mutual replacement of bases laid down by Professor Liebig. Supposing this law to be subject to no modification, and considering the accuracy of the analyses, we should have expected that in equal weights of the various ashes (the abnormal matters being deducted), the quantities of oxygen united to these bases would have been more nearly identical. In the case of plants containing much sap, this difference in the quantities of oxygen contained in the bases united to organic acids, is easily accounted for; partly by the reactions which we have already stated take place during the ignition of the ash, and partly by the influence which, as in the case of tobacco, the presence of nitrates, according to their quantity, will exert upon the amount of carbonates found in the ash.

The ashes of seeds, so far as their composition is known, consist, like those of the blood of man and other animals, principally of the phosphates of the alkalies and alkaline earths. The curious fact, moreover, has lately been observed, that the phosphoric acid is not in all seeds combined with the same number of equivalents of fixed base. Analyses conducted by ourselves and under our superintendence, show that peas, beans, horse beans, &c., that is, the Leguminosæ, and the seeds of the Coniferæ (the pines), &c., contain tribasic phosphates ($PO_5 + 3MO$). The seeds of the Cerealia (rye, wheat, millet,

buck-wheat, and also hemp and linseed) contain, on the other hand, bibasic phosphates ($PO_5 + 2MO$). This relation is maintained also when the seeds are grown in different localities. The solution of ashes containing tribasic phosphates gives a yellow precipitate with nitrate of silver, even if made immediately after ignition, whilst that of those containing bibasic phosphates gives a pure white precipitate. The quantities of oxygen contained in the bases of these seeds (deducting the sulphates and chlorides) are so nearly alike, that it is evident that the law of replacement of bases applies also to the phosphates. The following analyses demonstrate this fact.

I. *Analyses of Seed-Ashes containing tribasic phosphates, sometimes also mixed with bibasic phosphates.*

The analyses marked thus * were conducted under the superintendence of Dr. Will.

	Peas.			
	Fresenius and Will (Giessen).	Bichon (Holland).	Thon (Kurhessen).	Boussingault (Bechelbronn).
Potash	39·51	34·19	35·20	36·31
Soda	3·98	12·86	10·32	2·56
Lime	5·91	2·46	2·70	10·39
Magnesia	6·43	8·60	6·91	12·24
Peroxide of iron	1·05	0·96	1·94	
Phosphoric acid	34·50	34·57	34·01	31·00
Sulphuric acid	4·91	3·56	4·28	4·83
Chlorine (or chlor. sodium)	3·71	0·31	2·56	1·13
Silica	.....	0·25	0·29	1·54
Oxygen in the bases	11·18	12·23	11·44	13·51

	Horse-Beans (Vicia faba).			Beans (Phaseolus vulgare).	
	Bichon (Holland).	Boussing. (Alsace).	Buchner (Giessen).*	Thon (Kurh.).	Boussing. (Alsace).
Potash	20·82	47·14	32·71	21·71	51·36
Soda	19·06	.....	12·75	21·07	
Lime	7·26	5·33	4·72	5·38	6·07
Magnesia	8·87	8·98	6·13	7·35	12·03
Peroxide of iron	1·03	.....	0·66	0·34	
Phosphoric acid	37·94	35·67	39·11	35·33	28·53
Sulphuric acid	1·34	1·66	.....	2·28	1·36
Chlorine	1·48	0·71	.....	3·32†	0·10
Silica	2·46	0·51	0·47	1·48	1·05
Oxygen in the bases	13·56	12·42	12·69	13·04	14·73

† Chloride of sodium.

	Poleck.*			Muller.
	Scotch Fir.	Silver Fir.	Pinus Picea.	Brassica Napus.
Potash	22·37	18·57	21·75	21·34
Soda	1·26	5·78	6·76	5·26
Lime	1·86	1·54	1·54	14·63
Magnesia	12·57	16·79	16·79	11·96
Oxide of iron	2·51	1·31	1·31	2·84
Phosphoric acid	45·95	39·65	39·65	41·68
Chloride of sodium			0·57	.....
Silica	.....	0·57	11·71	1·52
Sulphuric acid	10·44	11·71	.....	0·77
Oxygen in the bases	12·94	.....	14·60	14·17

II. *Analyses of Seed-Ashes with bibasic phosphates.*

	Wheat.				
	Fresenius and Will (Giessen).		Bichon (Holland).	Thon (Solz in K.).	Boussingault (Bechelbronn).
	Red.	White.			
Potash	21·87	33·84	6·43	24·17	30·12
Soda	15·75	.....	27·79	10·34	
Lime	1·93	3·09	3·91	3·01	3·00
Magnesia	9·60	13·54	12·98	13·57	16·26
Peroxide of iron	1·36	0·31	0·50	0·52	
Phosphoric acid	49·32	49·21	46·14	45·53	48·30
Sulphuric acid	0·17	.....	0·27	.....	1·01
Chlorine (chlor. sodium)					
Silica	.....	.....	0·42	1·91	1·31
Quantity of oxygen in the bases	12·35	11·92	14·20	12·98	11·84

	Rye.		Buckwheat.	Maize.
	Fresenius and Will (Giessen).	Bichon (Cleve).	Bichon (Cleve).	Letellier (Bechelbronn).
Potash	32·76	11·43	8·74	30·8 & loss.
Soda	4·45	18·89	20·10	
Lime	2·92	7·05	6·66	1·3 ...
Magnesia	10·13	10·57	10·38	17·0 ...
Peroxide of iron	0·82	1·90	1·05	
Phosphoric acid	47·29	51·81	50·07	50·1 ...
Sulphuric acid	1·46	0·51	2·16	
Silica	0·17	0 69	0·69	0·8 ...
Quantity of oxygen in the bases	11·97	12·30	11·96	

	Bichon.	Poleck.*	Leuchtweiss.*		Boussing.
	Barley.	Millet.	Hemp-seed	Linseed.	Oats.
Potash	3·91	9·58	21·67	25·85	12·9
Soda	16·79	1·31	0·66	0·71	.....
Lime	3·36	0·61	26·63	25·27	3·7
Magnesia	10·05	7·66	1·00	0·22	7·7
Peroxide of iron	1·93	0·63	0·77	3·67	1·3
Phosphoric acid	40·65	18·19	34·72	40·11	14·9
Sulphate of lime	.....	0·60	0·18	1·70	
Chloride of sodium	.....	1·43	0·09	1·55	0·5
Silica	21·99	59·63	14·04	0·92	53·3
Sulphuric acid	0·26	.....	.....	.....	1·0
Carbon	.....	.....	.....	.....	4·7
Oxygen of the bases	11·70	.....	13·88	12·76	14·95

III. *Additional Analyses of Seed-Ashes.*

	Kleinschmidt. Acorn.*	Buch. Saintfoin.*
Potash	64·64	6·75
Soda	.....	20·33
Lime	4·89	
Magnesia	5·57	8·57
Peroxide of iron		
Phosphoric acid	15·62	54·89†
Sulphate of lime	4·73	2·87
Chloride of sodium	0·98	2·18
Silica	0·96	1·10
Phosphate of peroxide of iron	2·61	3·31

	Fruit of the Horse-chestnut. De Saussure.
Carbonate of potash	51
Phosphate of potash	28
Chloride of potassium and sulphate of potash	3
Earthy phosphates	12
Silica	0·5
Metallic oxides	0·25
Loss	5·25

It is of great importance that analyses should be made of the ashes of the most widely differing plants, and also of those of the same kind of plant grown on very different kinds of soil. This can only be accomplished, however, by the persevering cooperation of many chemists. The examples given above show how beautiful and fertile in their consequences are the results obtained by ash-analyses; and we hope that by means of the methods herein described, the work will be rendered somewhat more easy.

The difference in the solubility of the nitrogenous ingredients of the Leguminosæ, as regards their vegetable casein, and the nitrogenous ingredients of the Cereals, in respect of vegetable fibrin, arises evidently from the greater amount of alkaline bases contained in the seeds of the Leguminosæ, in comparison to the quantity of phosphoric acid, to which they have immediate reference. This larger quantity of base causes the

† Phosphate of lime.

solubility of the Leguminosæ in water, whilst the vegetable fibrin of the Cereals is insoluble therein. There is therefore ground for supposing that the phosphates are also bibasic in the Leguminosæ as well as in the Cereals; the third atom of the base would be consequently combined with the vegetable casein, and the tribasic phosphate be formed during the incineration.

The great quantity of sulphuric acid (from 3·5 to 4·9 per cent.) contained in the ashes of peas is remarkable in comparison to that of other seeds: in the ashes of beans it amounts to 2 per cent., in the ashes of wheat and rye to only 0·5 per cent., and is frequently altogether wanting. It is probable that the cause arises from the small quantity of phosphoric acid present, whilst the sulphur of the nitrogenous ingredients is more easily retained as sulphuric acid by the alkaline bases during the incineration. If fresh-prepared ashes from seed containing tribasic phosphates are exposed to the air, they take up carbonic acid. This is the reason why Boussingault* found in the ashes of horse-beans one per cent., and in that of the common beans 3·3 per cent. of carbonic acid.

Upon comparing the ashes of the wood of the apple-tree with that of the mistletoe growing from it, the difference in the quantity of potash and phosphoric acid contained in each is immediately evident: for whilst the ashes of the apple-tree wood contain only 19 per cent. of potash and 4 per cent. of phosphoric acid, we find that the ashes of the wood of the mistletoe contain double the quantity of potash and five times the quantity of phosphoric acid.

The mistletoe therefore appears to perform upon the tree the same functions (as far as regards the inorganic ingredients) as the fruit, in absorbing from the sap the phosphates. This is no doubt the cause of the injury produced on trees by parasitic plants. Further analytical investigations with this and other parasites will show whether this can be considered as a general law.

* *Economie Rurale*, t. ii. p. 327.

November 4, 1844.—The President in the Chair.

The following presents were announced to the Society's Library and Museum since the last Meeting:—

"Lectures on Agricultural Chemistry and Geology," by James F. W. Johnston, M.A., F.R.S., Parts 2, 3 and 4, from the author.

Johnston's "Elements of Agricultural Chemistry and Geology," from the author.

"Beiträge zur Physikalischen Chemie," von C. F. Schönbein, Professor of Chemistry in the University of Basle, from the author.

"On Isomeric Transmutation," by G. Wilson, M.D., from the author.

"Journal of the Franklin Institute," No. 1, vol. viii., from the editor.

"An Inaugural Lecture on Chemistry," read at Queen's College, Birmingham, October 7, 1844, by Thomas G. Tilley, Ph.D., from the author.

"First Report of the Health of Towns' Commission," Parts 1 and 2, vol. i.

Four Pictures taken by his Energiatype process, from Robert Hunt, Esq.

A Specimen of Butter, supposed to be 300 years old, discovered in a Bog near Downpatrick in June 1844, from John F. Hodges, M.D.

Numerous Specimens of Organic Compounds and Salts, from Frederick C. Calvert, Esq.

A Specimen of Tartrate of Antimony and Potash in large Crystals, from M. Scanlan, Esq.

Remigius Fresenius, M.D., was elected a Foreign Member of the Society; and James Sheridan Muspratt, Ph.D., Robert Hunt, Esq., and E. H. Durden, Esq., were elected Members.

Mr. Reekes exhibited a Specimen of Etching on Steel by Galvanic Electricity, as described by Mr. Pring.

The following communications were then read:—

A Letter from Mr. Charles F. Burnard, describing a Modification of the Apparatus for Estimating the Carbonic Acid in Carbonated Alkalies, &c.

"On the Analysis of the Mineral Water of Bonnington, near Leith, Scotland," by E. G. Schweitzer, Esq., was commenced.

CXV. *Examination of a Specimen of diseased Wheat.* *By* Mr. J. Carty.

MY attention was lately directed by Mr. Briggs, of Overton, near Wakefield in Yorkshire, to a kind of disease which he considers to be burnt ear, and analogous to smut, which had attacked some wheat growing on his land. The stalk of the wheat was of the usual height and strength, and the ears seemed externally healthy; but on breaking into the grain it was found to be filled with a black powder, instead of the white, thick juicy substance found in healthy wheat at the

same period of growth. It was a thick-set red wheat, sown in December on a light and good turnip soil, to which an unusually large quantity of guano (4 cwt. per acre) had been applied as a manure. About one-tenth of the whole quantity was diseased, while several other kinds of wheat, sown in the same field, but to which no guano had been applied, were perfectly sound.

The ears had a much greener appearance than the same kind of wheat in a healthy condition, and emitted a very disagreeable smell, which is not easily described.

On close examination the grains were found filled with a black unctuous powder in place of the milky pulp of the healthy seed. This powder was separated in quantity by bruising the ears in a mortar and sifting through fine muslin, and submitted to chemical examination. It had the same disagreeable smell as the ears, but stronger; it was oily to the touch, and heavier than alcohol and water. When heated in the air it burned with a bright flame, leaving a residue of charcoal, and eventually a trace of white ash. When heated in a tube, it gave off water, empyreumatic and oily matters, and a little ammonia. It was insoluble in a solution of potash and in hydrochloric acid; nitric acid made it yellow, and hot sulphuric acid dissolved it with purplish-red colour. Boiled with water, it yielded merely a little gum and bitter brown extractive matter, the greater part remaining undissolved. Alcohol extracted a fat oil, and a waxy or resinous matter; the undissolved portion appeared to consist of lignin mixed with charcoal. The black powder greedily absorbed oxygen from the air when in a moistened condition, giving rise to carbonic acid.

A carefully conducted proximate analysis of the substance led to the following results:—

Wax or resin with fixed oil . . .	7·0
Gum and extractive matter, &c. .	7·8
Lignin and charcoal	82·7
Ashes	2·5
	100·

The ash consisted chiefly of earthy phosphates and silicate of potash.

November 18, 1844.—Thomas Graham, Esq., Vice-President, in the Chair.

J. J. Griffin, Esq., presented to the Society's Library Davy's "Elements of Agricultural Chemistry, by John Shier, A.M.," and a Series of Chemical Labels.

"Taylor's Calendar of the Meetings of the Scientific Societies of London for 1844 and 1845," was presented by the editor.

Specimens of Purreic Acid and of Purrenone were presented by John Stenhouse, Ph.D.; and a Specimen of the Purree or Indian Yellow, and of Sulphate of Soda in fine crystals, by Robert Warington, Esq.

Mr. Robert Murray exhibited experimentally the phænomenon of the sound produced in a bar of soft iron at the moment of making and breaking contact with a single galvanic arrangement in connection with a coil passing round the bar, but not in contact, as originally observed by Mr. Joule, and lately described by Mr. J. P. Marrian*.

The following communications were then read:—

CXVI. *Analysis of the Bonnington Water, near Leith, Scotland. By* Edward G. Schweitzer, *Esq.*

THE soil from which this mineral spring rises, according to the kind information obtained through G. Haig, Esq. of Bonnington House, is, for 20 feet below the surface, a wet, slipping sand of a yellowish colour, which is succeeded, for 20 feet, by a black hard clay, and this is followed, by a hard sandstone rock of considerable thickness, limestone of different qualities, and two small seams of coal; these have been bored, with very little interruption, through the extent of 184 feet. The mineral water when taken from the spring is quite transparent, with an empyreumatic smell, which it likewise imparts to the palate; it has also the taste of alkaline chlorides and iron. When a bottle containing the water for examination was opened, no disengagement of carbonic acid gas was perceptible, and when poured into a glass vessel but few bubbles of gas appeared at the sides; when mixed, however, with an acid, a slight discharge of carbonic acid gas took place. When exposed to the atmospheric air it becomes turbid, and a brownish sediment is formed; a few dark brown flakes were also floating in it, which were separately examined. The natural temperature of this water is about 44° Fahr., its specific gravity at 60° F. is 1·002618, and the quantity emitted from the spring amounts to about from 4 to 5 gallons per minute.

It indicated no action upon blue litmus paper; when boiled it became turbid, oxide of iron with some organic matter precipitated, and a slight alkaline reaction upon reddened litmus paper was developed. The usual well-known application of tests for a qualitative analysis evidenced the presence of potassa, soda, lime, magnesia, oxide of iron, sulphuric acid, chlorine, and carbonic acid gas.

* Phil. Mag., vol. xxv. p. 382.

A portion of the water was concentrated by evaporation and divided into two parts; one of which, on being treated with fresh starch-paste and nitric acid, gave indication of iodine; the other part, when freed from iodine by nitric acid and æther, was mixed with a solution of chlorine and æther, which proved the existence of bromine. Nitrate of silver added to the mineral water gave a precipitate of chloride of silver, which became gray and afterwards purple, indicating organic matter, which was obviously demonstrated by the residue, after evaporating some of the water to dryness, becoming charred during ignition. Acetate of lead gave a yellowish-white precipitate, proving the absence of hydrosulphuric acid. Caustic soda disengaged ammonia in abundance, which was evinced even by carbonate of soda.

The ingredients, which are present in very small quantities, were determined during the quantitative analysis, where a large volume of the water is evaporated, and consequently their detection rendered more easy.

It may not be irrelevant to mention an excellent test for nitric acid, when accompanied either by iodine or bromine, or both, its value being enhanced by the following results made respecting its action. It is known that the presence of nitric acid is easily indicated, when, to the concentrated fluid to be examined, pure sulphuric acid is added, and to this mixture a concentrated solution of the proto-sulphate of iron. The smallest trace of nitric acid, even the $\frac{1}{4000}$th or $\frac{1}{3000}$th part, is evidenced by the appearance of a pink colour, more or less intense. A large amount of nitric acid is indicated by a black colour, a combination of the oxide of nitrogen with the protoxide of iron; however, here we have only to consider minute proportions. The salts of iodine and bromine, when treated with the same test, tinge the fluid with their own peculiar colour, but a greater addition of the solution of the proto-sulphate of iron destroys the colouring, which is not the case with nitric acid. If the quantity of nitric acid be very small, and that of iodine predominates, it is necessary for comparison to make a standard fluid, from which not only the presence of nitric acid may be inferred with certainty, but even its approximate quantity. For that purpose I employ 50 grs. of distilled water in which half a grain of iodide of potassium is dissolved, to this I add gradually 50 grs. of sulphuric acid, and afterwards 50 grs. of a concentrated solution of proto-sulphate of iron. The sulphuric acid precipitates the iodine, which is redissolved by the addition of the iron solution—forming an iodide of iron—whereby the fluid assumes a yellowish tinge, resembling the colour of a solution of chromate of potassa;

the smallest proportion of nitric acid, however, should it even amount to $\frac{1}{3000}$th part, will in this diluted state be manifested by a brownish tinge, which becomes much darker in proportion as the quantity of nitric acid increases. If a bromide be present instead of an iodide, the nitric acid can be ascertained with equal facility, from its imparting a greenish tinge to the fluid. 50 grs. of distilled water containing half a grain of an alkaline bromide to which 50 grs. of sulphuric acid have been added, will indicate $\frac{1}{2000}$th part of nitric acid, by developing a brownish tinge, whereas a similar mixture without the nitric acid will remain colourless. This is obvious, as in the first instance, by the addition of the sulphuric acid, hydrobromic acid is formed, which is colourless, but becomes again decomposed by the presence of free nitric acid, whereby the fluid contracts a brownish tinge. The presence of both bromides and iodides does not interfere with the delicacy of this test for nitric acid, the reaction is the same as if an iodide only were present. However sure and delicate this test is, the presence of organic matter makes it complicated, and where the organic matter cannot be perfectly separated, the presence of nitric acid is easily overlooked, which indeed happened in this analysis at the first examination. In such cases I find the test with indigo* preferable; yet, where the quantity of nitric acid is very small, it is best to submit the concentrated fluid to distillation with sulphuric acid, as mentioned hereafter in the quantitative analysis, by which process the nitric acid was estimated.

It is obvious that a mineral water, containing a great number of ingredients, has to undergo a series of processes for the purpose of ascertaining the individual quantity of each, by which elaborate proceedings small proportions of them might be lost. It is therefore of paramount necessity to have, not only at the commencement of the analysis, but also during its progress, a means of control, which will confirm the correctness of the results of the analysis, and it is chiefly with this view that I have edited this paper.

Alkaline mineral waters which have no volatile ingredients, such as ammonia, are to be controlled, regarding the total amount of their ingredients, by merely evaporating the water and igniting the residue; but if the water contains chiefly chlorides, and particularly earthy chlorides and chloride of ammonium, the mere evaporation, at a temperature approaching the boiling-point, is sufficient to drive off hydrochloric acid, and even ammonia, and if the water contains organic matter the control becomes still more difficult. As the Bonnington water presents these difficulties, they shall be pointed out du-

* Rose's *Handbuch der Analytischen Chemie*, Band i. p. 235.

ring the progress of the examination. It is indeed, under all circumstances, a very safe and necessary proceeding, to ascertain the weight of all the solid ingredients, and also the weight of some of the electro-negative substances, such as sulphuric acid, chlorine, &c. This will give a proper control for those results which are afterwards obtained from the evaporated water. For this purpose,

1. Four troy ounces (=1920 grs.) of the water were supersaturated with hydrochloric acid, and, when boiling*, precipitated by chloride of barium.

a. Experiment gave 3·622 grs. of sulphate of barytes.

b. ... ... 3·602 grs. ... ...

The average = 3·612 grs., making for 16 troy ozs. of water 14·448 grs.

2. Four troy ounces of the water acidulated by nitric acid gave a precipitate with nitrate of silver, weighing—

a. Experiment . . . . . 10·030 grs.
b. ... . 10·077 grs.
The average = 10·053 grs.

This precipitate however had been influenced by the organic matter, but this will be noticed again hereafter.

3. To ascertain the total amount of the solid ingredients, 1000 grs. were evaporated in a platina crucible, the residue dried at various temperatures, and the weight taken, when no further diminution was perceptible. The heated crucible was cooled over sulphuric acid, and then quickly weighed; a proceeding followed throughout the course of the analysis. The results were as follows:—

a. Residue† dried at 212° Fahr. gave 3·712 grs.

b. ... dried at 300° to 310° Fahr. gave 3·311 grs.

c. ... heated over a spirit-lamp till the evaporation of the ammonia had ceased, and as long as the escape of hydrochloric acid was perceptible, gave 2·339 grs.; from the charring of the organic matter the mass appeared black.

d. Residue heated to incandescence until the organic matter had been burned away, leaving the residue almost white, gave 2·123 grs.

From the above statement it is obvious that a very exact result cannot be obtained regarding the amount of the solid ingredients. The earthy chlorides require for their existence

* It facilitates very much the separation and lixiviation of the sulphate of barytes, when it is precipitated from a boiling menstruum, and the particles are thereby prevented from penetrating the pores of the filter.

† This residue when placed in a humid atmosphere attracted water and became half fluid.

a small proportion of water. Experiment *a* gives therefore a wrong result, as they still contain this water, but in depriving them of it at a higher temperature some hydrochloric acid would be set free; moreover, as the existence of ammonia has been proved, it is impossible to dry the residue without a small loss of chloride of ammonium, so that experiment *b* must give a result too low. Yet the truth of the result must lie within the limits of the experiments *a* and *b*. The last two experiments, *c* and *d*, from the destruction of organic matter, and the evolution of ammonia and hydrochloric acid, can be no guide whatever. An excellent control, which I frequently apply in various analyses, is to change the chlorides, carbonates, &c. into sulphates; the total amount of the latter must closely approach the amount of the various ingredients obtained by analysis when computed as sulphates. This is a very satisfactory proceeding, and must give a correct result if the water does not contain ammonia, oxide of iron or alumina; the ammonia, however, being dissipated by heat must be deducted from the total amount of ingredients obtained by analysis, and as the oxide of iron and alumina (both losing a large quantity of sulphuric acid during ignition) are generally present in very small quantities, they will still allow of the above proceedings; but should they amount to any considerable quantity, as in some chalybeate and aluminous waters, this mode of control is not applicable. The residue which was derived from experiment 3 *d*, amounting to 2·123 grs., was heated in a platina crucible with a sufficient quantity of sulphuric acid and ignited at a red heat, until all the ingredients were changed into neutral sulphates; it yielded 2·663 grs.

After these preliminary examinations the *quantitative analysis* was perfomed.

76·800 grs. were evaporated in a porcelain basin * with a proportionate quantity of chemically pure carbonate of soda, sufficient to decompose the earthy chlorides and sulphates. The application of carbonate of soda, besides preventing the escape of hydrochloric acid, affords another advantage, namely, it counteracts the formation of sulphate of lime, which is a very troublesome ingredient, inasmuch as it adheres closely to the vessel, and small quantities are not easily visible in a white porcelain basin; moreover, it is not soluble in hydrochloric

* The dark brown flakes which were floating in the water were collected and analysed by themselves, with the rinsing obtained from the glass bottles by hydrochloric acid, any oxide of iron that might adhere to the sides of the bottles being thus dissolved. The water contained only a small proportion of iron in solution.

acid, and requires 461½ parts of water to re-dissolve it, whereas by the addition of carbonate of soda, the earthy carbonates, hereby produced, do not present any difficulty. For the above quantity of water it was found requisite to add 201·123 grs. of anhydrous carbonate of soda*; the whole was evaporated in a water-bath until a few ounces of fluid remained. It was then placed upon a filter, and the earthy residue A lixiviated with boiling water till the filtered liquor gave no indication of sulphates and chlorides. The fluid obtained from the edulcoration of the earthy residue A was evaporated, when some earthy particles were again separated, which were collected upon a filter B. It is here to be noticed, that by this method it is impossible to separate, with any degree of accuracy, the earthy ingredients from the soluble ones, as, by edulcoration, a small proportion of the former will always be re-dissolved; and however often this process may be repeated, whereby the quantity of the re-dissolved earthy ingredients will certainly be diminished, still the last traces of them cannot be obtained; moreover, the repeated evaporation of the lixiviating fluid must carry with it the unavoidable chances of loss: I therefore ascertain these traces of earthy ingredients by themselves along with the soluble salts. A small portion of the earthy carbonates adhered to the sides of the evaporating vessel; these were removed by hydrochloric acid, and the acid solution C, hereby obtained, was left with the other earthy ingredients, A and B, for further examination.

I. *Quantitative Analysis of the Soluble Ingredients.*

The fluid containing the soluble salts, and the edulcorating fluids † obtained from the earthy ingredients, were evaporated to the weight of 8100 grs.

1. *Earthy ingredients.*—One-tenth of the fluid (810 grs.) was evaporated to dryness and the residue submitted to various temperatures, when the following results were obtained:—

At 212° Fahr.	31·352 grs.
At 260° to 280° Fahr.	31·051 grs.
Ignited and fused over a spirit-lamp till the organic matter was destroyed	30·580 grs.

* By adding the carbonate of soda in solution to the mineral water, it is requisite to ascertain very exactly its quantity in the anhydrous state; the best method I found is to change the carbonate into a sulphate, and to ignite the latter in an atmosphere of carbonate of ammonia, so as to discharge any possible surplus of sulphuric acid. If the carbonate of soda be ascertained as a carbonate, it must *always* be fused and quickly weighed.

† It is always advisable to evaporate first the edulcorating fluids, and when properly concentrated, to mix them with the fluid which chiefly contains the dissolved ingredients.

This residue was dissolved in water and effervesced by the addition of hydrochloric acid; it was evaporated, the residue moistened with hydrochloric acid, and after a few hours again dissolved in water, when a scarcely visible sediment separated. The acid fluid was supersaturated with ammonia; oxalate of ammonia gave no indication of lime, but phosphate of ammonia gave a small precipitate of the ammonio-phosphate of magnesia; this was edulcorated upon a filter with dilute ammonia, which prevents the re-solution of this salt, dried and ignited it gave 0·0309 gr.* of phosphate of magnesia, equivalent to 0·011 magnesia. Another mode of Berzelius, which gives likewise very exact results, I will briefly notice. The concentrated solution of the alkaline chlorides is to be evaporated to dryness with oxide of mercury. The chloride of magnesium is changed into magnesia, and chloride of mercury is produced, which latter unites with the alkaline chlorides. The further process is obvious†.

2. *Sulphuric acid.*—One-twentieth part of the fluid containing the soluble ingredients was acidulated by hydrochloric acid, and when boiling precipitated by chloride of barium. The sulphate of barytes weighed 7·201 grs., which amounts upon 16 ozs. troy to 14·403 grs., equivalent to 4·950 grs. of sulphuric acid. If we compare this result with the one obtained by the preliminary experiments at 1, it will be seen that it closely agrees.

3. *Nitric acid.*—810 grs. of the fluid containing the soluble ingredients were very carefully neutralized by dilute sulphuric acid and macerated with a due proportion of sulphate of silver, in order to change the chlorides, iodides and bromides into sulphates‡. The fluid separated from the silver precipitate was made alkaline by a little carbonate of soda, concentrated in a water-bath to a few ounces, and mixed in a tubulated retort with an adequate quantity of chemically pure sulphuric acid (previously boiled), more than sufficient to convert all the ingredients into bisulphates. This mixture was heated in a sand-bath and the vapours conducted into a glass receiver containing a solution of hydrate of barytes, and the distillation interrupted as soon as fumes

* I have to notice that I used the French gramme for ascertaining the weight of the ingredients, which I applied with precision to the first decimal number of a millegramme.

† See Berzelius's *Jahresbericht*. 21st Jahrgang, 2nd Theil.

‡ A fluid containing a large amount of chlorides would require a very considerable quantity of the solution of sulphate of silver, inasmuch as this salt requires a great deal of water for its solution. To avoid this it is only necessary to mix the diluted fluid with the sulphate of silver, which has been previously triturated in a mortar with water, and to leave it for some time in a temperature not exceeding 100° F.

of sulphuric acid appeared. The fluid thus obtained was evaporated in a water-bath nearly to dryness, and the residue left for twelve hours exposed to the atmospheric air, in order to change the excess of hydrate of barytes into a carbonate*. After the separation of the carbonate of barytes the fluid was mixed with sulphuric acid, when 2·416 grs. of sulphate of barytes were obtained, equivalent to 1·1220 gr. of nitric acid.

4. *Chlorine.*—One-twentieth part, equal to 405 grs., of the fluid containing the soluble ingredients was evaporated, and the residue fused to destroy the organic matter, and again dissolved. The solution supersaturated with nitric acid was precipitated by nitrate of silver. The precipitate was carefully collected upon a filter and lixiviated, first with water slightly acidulated with nitric acid, and afterwards with pure water. The dried precipitate was heated nearly to the point of fusing in a well-covered porcelain crucible, when 19·388 grs. of chloride of silver was obtained, making for 16 ozs. troy of water 38·776 grs.; but, as will be seen hereafter, 0·126 gr. of bromide of silver and 0·010 gr. of iodide of silver are to be deducted from the amount (38·776 − 0·136), leaving 38·640 grs. of chloride of silver, equivalent to 9·533 grs. chlorine. If we compare the amount of the silver precipitate with that obtained from the preliminary experiment 2, we find a slight difference; the latter giving from two experiments in 4 ounces 10·053 grs., whereas the former, calculated upon the same quantity of water, gives 9·694 grs. This discrepancy is accounted for, from the organic matter in the original water being partly thrown down with the silver precipitate. It is therefore requisite to free the fluid from its organic matter before the amount of its chlorides can be ascertained. The interference of organic matter with correct results is evidenced by the following experiments:—

a. Four troy ounces of the fresh water gave with nitrate of silver 10·053 grs.

b. Four troy ounces of the water evaporated with carbonate of soda and freed from the earthy carbonates†, gave with nitrate of silver 9·883 grs.

c. Four troy ounces of the water evaporated with carbonate of soda and freed from the earthy carbonates, the filtered liquid again evaporated, the residue fused and again dissolved, gave with nitrate of silver 9·694 grs.

5. *Iodine.*—4860 grs. of the fluid containing the soluble in-

* It is advisable to evaporate the fluid twice nearly to dryness, and filter each time, and to use for lixiviation as little water as possible, so as to prevent the solution of the carbonate of barytes.

† A portion of the organic matter followed the earthy carbonates.

gredients were evaporated to dryness and the residue boiled four times with an adequate proportion of alcohol. [The residue after extraction showed no trace of iodine or bromine.] The alcoholic fluid was evaporated in a retort till an ounce remained, which, with the addition of a few grains of carbonate of soda, was evaporated to dryness in a platina crucible, the residue gently heated to a low red heat for the purpose of destroying the organic matter, again dissolved in water and filtered. The alkaline fluid thus obtained was very carefully neutralized by dilute hydrochloric acid; it held now in solution the whole amount of iodine and bromine. In my account of the analysis of the sea-water in the British Channel*, I described my method for separating iodine from bromine and chlorine. This method, though accurate, is more tedious than the method of Lassaigne, which was published after I had written that analysis. Lassaigne recommends to precipitate the iodine by chloride of palladium, and of this excellent and approved test I availed myself. Protochloride of palladium was added to the above fluid, which became at first turbid, but after the lapse of ten hours transparent, and a black-brown precipitate of protoiodide of palladium was obtained, which, when collected upon a filter, lixiviated and dried at 212°F., amounted to 0·046 gr., equivalent to 0·060 gr. of iodide of silver, making for 16 troy ozs. of water 0·010 gr. of iodide of silver, equivalent to 0·005 gr. of iodine.

6. *Bromine.*—The fluid obtained after the separation of the protoiodide of palladium was saturated with hydrosulphuric acid gas to remove the excess of the palladium salt. Having separated by filtration the sulphuret of palladium the fluid was evaporated, the residue dissolved, the fluid filtered and concentrated by evaporation; to this solution was added a few drops of an ammoniacal solution of chloride of silver prepared thus: one part of a saturated solution of chloride of silver in ammonia, mixed with one part of ammonia and one part of water. A few drops of this mixture produced no turbidity in a saturated solution of chloride of sodium, but would indicate a very minute quantity of bromine. I refer for the further proceeding to my analysis of the sea-water in the British Channel. By this process 0·759 gr. of bromide of silver were obtained, making for 16 ozs. troy 0·126 gr., equivalent to 0·053 gr. of bromine.

7. *Potassa.*—810 grs. of the fluid containing the soluble ingredients were neutralized by hydrochloric acid and the sulphuric acid precipitated by chloride of barium. After the separation of the sulphate of barytes, the fluid was mixed

* See the London and Edinburgh Philosophical Magazine, No. 93, July 1839.

with carbonate of ammonia and evaporated nearly to dryness, to free it from the surplus of the barytes salt. Having separated the carbonate of barytes, the fluid thus obtained was evaporated, and the residue heated to fusion in a well-covered crucible. The alkaline chlorides were dissolved in water and mixed with a surplus quantity of perchloride of platinum, and evaporated in a temperature of 175° F. nearly to dryness; the residue was macerated with spirits of wine (containing 60 per cent. of alcohol) as long as anything dissolved, when potassio-chloride of platinum was left behind weighing 6·036 grs., equivalent to 1·167 gr. potassa.

8. *Soda.*—The usual way of ascertaining the amount of soda is by an indirect method. This has no difficulties with alkaline mineral waters; the amount of soda is obtained when the whole amount of the ingredients found by analysis in the fluid containing the soluble salts is deducted from the whole weight of the alkaline salts obtained by evaporation; however, this method cannot be applied where mineral waters have no alkaline carbonates, and where carbonate of soda has been added to the water, which by the presence of earthy chlorides, &c. has been rarely changed into chloride of sodium.

The following method I employed here for ascertaining the soda by calculation:—It is requisite to arrange the ingredients established by analysis into binary combinations. Potassa, as the strongest and only base* ascertained, is united to sulphuric acid, and the surplus of the latter with the other electro-negative ingredients must therefore have been in combination with soda. The nitric acid has existed as nitrate of soda; this acid, however, in conjunction with organic matter at the high temperature at which the soluble ingredients were fused, has become decomposed, forming with soda carbonate of soda, an assumption established by facts.

	grs.		grs.
1.	1·167 potassa give		2·158 sulphate of potassa.
2.	4·950 sulphuric acid,		
	less 0·991 united with potassa,		
	leaves 3·959 sulphuric acid, give		7·047 sulphate of soda.
3.	1·122 nitric acid give		
	1·7697 nitrate of soda,		
	equivalent to		1·106 carbonate of soda.
4.	9·533 chlorine give		15·798 chloride of sodium.
5.	0·005 iodine give		0·006 iodide of sodium.
6.	0·053 bromine give		0·069 bromide of sodium.
7.			0·011 magnesia.
		Total	26·195

* With the exception of a small quantity of magnesia which was united to soda.

It will be seen, however, that the total amount of all the ingredients in an anhydrous state obtained at 1, by the analysis of the earthy bases existing in the soluble salts, amounted to 30·580 grs.; deducting the above amount, 26·195 grs., there remains 4·385 grs. carbonate of soda, which is left unchanged of that quantity of carbonate of soda which was originally added to the mineral water when evaporated. If the soda added to 16 troy ozs. of the water be now deducted from the whole amount of the soda obtained by calculation, the exact quantity of soda existing in the water will be then ascertained.

7·047 grs.	of sulphate of soda	= 3·088	soda.
1·106 ...	carbonate of soda	= 0·648	...
15·798 ...	chloride of sodium	= 8·418	...
0·006 ...	iodide of sodium	= 0·001	...
0·069 ...	bromide of sodium	= 0·021	...
4·385 ...	carbonate of soda	= 2·569	...
	Total .	14·745	grs.
Carbonate of soda added 20·11230 grs. =	soda	11·782	...
Leaving for soda existing in 16 troy ounces of mineral water		2·963	...

According to the foregoing analysis, the following soluble ingredients are obtained in 16 ounces troy of the water:—

	grs.
Potassa	1·167
Soda	2·963
Magnesia . . .	0·011
Sulphuric acid . .	4·950
Nitric acid . . .	1·122
Iodine	0·005
Bromine . . .	0·053
Chlorine . . .	9·533
Total .	19·804

II. *Analysis of the Earthy Ingredients.*

By separating the soluble ingredients from the earthy carbonates, the precipitates A and B were obtained, and also an acid fluid C, which was boiled with an adequate quantity of carbonate of soda, the precipitate thrown down, well-lixiviated, placed in conjunction with A and B in a platina crucible*, and submitted to a temperature of 280° to 300° F. until

* Every filter was dried in a platina crucible at 212° F., cooled over sulphuric acid, and its weight quickly taken in the same well-covered crucible. Where the nature of the precipitate or other circumstances did not admit of the combustion of the filter, I found it in most cases advantageous to remove the contents of the filter, still half-moist, into a crucible, and to wash the last traces from the filter with a washing bottle.

its weight did not alter; it gave 84·301 grs. The earthy carbonates were now dissolved very carefully in nitric acid, great care being taken that no loss was sustained during the effervescence, which is best obviated by covering the vessel with a convex glass, having in its centre a very small aperture for admitting the dilute acid to drop gradually into the vessel. The solution thus obtained was evaporated in a water-bath to dryness, (no action upon the glass that covered the platina vessel was perceptible, manifesting the absence of fluates,) moistened with nitric acid, and left in that state for twelve hours, when it was re-dissolved. The substance which did not dissolve was lixiviated and boiled with hydrochloric acid, which left a perfectly white silica (*a*), weighing 1·509 gr*. The acid fluid from *a* was then carefully neutralized with ammonia, and, under the well-known precautions, precipitated by succinate of ammonia; the precipitate was first lixiviated by very dilute ammonia, and afterwards with pure water, then carefully ignited with free exposure to the air, when 0·105 gr. of oxide of iron (*b*) was obtained. The fluid derived from *b* was precipitated by hydrosulphate of ammonia; the precipitate, dissolved in hydrochloric acid and boiled with an adequate quantity of carbonate of soda, gave a precipitate, which, after lixiviation with boiling water and ignition, weighed 0·059 gr., and was red oxide of manganese (*c*). The acid fluid obtained from D was mixed in a closed vessel with ammonia, and after the precipitate had subsided, the supernatant fluid was quickly filtered, protected from the atmospheric air, and the precipitate (E), lixiviated and ignited, weighed 11·819 grs. The menstruum from which this precipitate was obtained was only slightly acid, so that but a small amount of an ammonia-salt could be formed, and hence a larger amount of magnesia was precipitated, as will be hereafter seen. The precipitate (E) was dissolved in hydrochloric acid; it left 0·103 gr. silica (*d*). The filtered fluid was mixed with bicarbonate of potassa, when a precipitate (F) was formed. This precipitate was dissolved in hydrochloric acid, and the solution boiled with caustic soda; the precipitate (G) thus formed, after lixiviation, was redissolved in hydrochloric acid and precipitated by ammonia, when 0·244 gr. oxide of iron (*e*) was obtained, which dissolved in hydrochloric acid without residue and gave no indications of manganese. The menstruum from which this oxide of iron was precipitated gave with hydrosulphate of ammonia a few minute flakes of sulphuret of

* Very often the silica cannot be easily freed from traces of iron: in such cases it is requisite to fuse it with three or four times of its weight of carbonate of soda, and to dissolve it afterwards in hydrochloric acid.

manganese, scarcely to be weighed. The caustic fluid* obtained from G was supersaturated by hydrochloric acid, when ammonia gave a precipitate (*f*) of 0·134 gr. of alumina. The filtered fluid from the alumina was evaporated to dryness; the residue, after being heated till the ammoniacal salt was dissipated, left, when dissolved in water, a small trace (*g*) of alumina, weighing 0·063 gr.† The fluid obtained from the precipitate (F) was neutralized by hydrochloric acid, and quickly evaporated with carbonate of potassa, and when nearly dry mixed with boiling water and filtered; the precipitate (F) having been properly edulcorated with boiling water, weighed after ignition 10·857 grs., it was redissolved in hydrochloric acid and treated with hydrosulphate of ammonia; the precipitate hereby obtained was collected upon a filter, and gave after a similar treatment as *c*, 0·043 gr. oxide of manganese (*h*); deducting this amount from 10·857, there remains 10·809 grs. of magnesia (*i*)‡, equal to 22·372 grs. of carbonate of magnesia. The fluid obtained from the precipitate (F) still contained some traces of magnesia, it was therefore precipitated by ammonia and phosphate of ammonia, when the precipitate, after lixiviation with dilute ammonia and ignition, gave 1·127 gr. of phosphate of magnesia, equivalent to 0·413 magnesia (*k*), equivalent to 0·854 gr. carbonate of magnesia. The ammoniacal fluid obtained from the precipitate (E) was next precipitated by oxalate of ammonia, and as soon as the precipitate had settled it was quickly filtered and lixiviated§. This precipitate (I) was ignited under the well-known pre-

* As caustic potassa or soda is seldom if ever quite free from traces of silica or alumina, I ascertain, previous to the application of these tests, the quantity of the latter, for which a due deduction is made.

† I have here to observe, that every ingredient obtained was, after its weight had been ascertained, again examined for its purity. The alumina, as well as the oxide of iron, was examined before the blowpipe for phosphoric acid; besides, these precipitates were dissolved in hydrochloric acid, precipitated by ammonia, and re-dissolved by a gentle heat in acetic acid, when after the lapse of one day no sediment had formed, evidencing the absence of phosphoric acid. The caustic fluid from which the last trace of alumina was separated was likewise tested for phosphoric acid, by adding to the fluid, neutralized by hydrochloric acid, chloride of calcium; but no trace of it was discernible.

‡ It is very difficult to separate the last traces of magnesia by carbonate of potassa; the fluid should be boiled quickly to dryness, and the residue lixiviated by boiling water. The fluid obtained from the residue should invariably be examined if it is free from magnesia. As in the above process the fluid containing the magnesia was not boiled to dryness, it accounts for the larger amount of magnesia obtained afterwards.

§ When magnesia and lime are to be separated, both in considerable quantity, it is requisite to have the menstruum well-diluted, and to filter the oxalate of lime as soon as possible without interruption, so as to prevent the admixture of oxalate of magnesia.

cautions for carbonate of lime, when it weighed 40·579 grs.; it was again dissolved in nitric acid, when 0·005 gr. silica (*l*) was left. The solution of nitrate of lime gave no indications of manganese nor of strontia when the nitrate was changed into a chloride. [If earthy carbonates be dissolved in nitric acid, and tested for strontia by sulphate of lime, small quantities are not detected, but when the carbonates are changed into chlorides minute proportions are easily evidenced by that test.] Deducting 0·005 from 40·579, there remains 40·574 grs. of carbonate of lime (*m*). The filtered fluid derived from (I) was now examined for magnesia. The simplest method would be to evaporate the fluid to dryness, and to ignite the residue until the ammoniacal salts are dissipated; however, this offers some difficulties, particularly as the mass on approaching the dry state rises and involves the probabilities of loss. It is therefore an advisable method to halve the fluid, and ascertain the quantity of magnesia in the one part by phosphate of ammonia, and in the other by evaporation, by which latter process also a few other ingredients, in very small quantity, which have hitherto escaped, may be found. One portion yielded, when precipitated by phosphate of ammonia, &c., 10·344 grs. phosphate of magnesia, equivalent to 3·793 of magnesia. The other half was evaporated to dryness and the residue ignited, when it left 4·186 grs. of a perfectly white magnesia. This was boiled with water, which left after evaporation 0·370 gr. of carbonate of soda (*n*), equivalent upon the whole mass to 0·740 gr. When re-dissolved it acted strongly upon turmeric paper, effervesced with acids, and gave a very minute crystalline precipitate with perchloride of platinum, indicating that the soda contained a slight admixture of potassa. The soda was derived from a soda-carbonate of magnesia, which became decomposed by ignition, and from which boiling water extracted the soda*. The residue from which the carbonate of soda was separated was dissolved in hydrochloric acid, when again a small proportion of 0·010 gr. silica was left, making the whole silica 0·020 (*o*). If the amount of silica (0·010) and that of soda (0·370) is deducted from 4·186, there remains 3·806 grs. of pure magnesia, which upon the whole gives magnesia 7·612 grs. (*p*), equivalent to 15·759 carbonate of magnesia; this amount corresponds very closely with that obtained by the first experiment. The amount therefore of earthy ingredients obtained by analysis stands thus:—

* By performing the latter method of ascertaining magnesia, it is indispensably necessary to examine the oxalate of ammonia, which frequently yields after ignition traces of alkaline carbonates.

	grs.
Silica (*a*, *d*, *l*, *o*)	1·637
Oxide of iron (*b*, *e*)	0·349
Oxide of manganese (*c*, *h*)	0·107
Alumina (*f*, *g*)	0·197
Carbonate of magnesia (*i*, *k*, *p*) . . .	38·985
Carbonate of lime (*m*)	40·574
Carbonate of soda (*n*)	0·740
Total	82·589*

III. *Analysis for the Carbonic Acid Gas and Ammonia.*

1. *Carbonic acid gas.*—Before the above ingredients are computed to binary combinations, we have to ascertain the amount of carbonic acid gas and of ammonia. It is obvious that these two ingredients could not be ascertained from the evaporated water, and therefore new quantities of the mineral water had to be taken. For the analysis of the first 2880 grs. (=6 ounces troy) of the water were precipitated by chloride of barium, and the precipitate collected upon a small filter; this, while still wet and properly compressed, was introduced into a graduated tube over mercury with an adequate quantity of hydrochloric acid, previously saturated with carbonic acid gas. Having made a due reduction for the elasticity of the aqueous vapour, &c., 0·300 gr. were obtained, making for 16 ozs. 0·802 gr. of carbonic acid gas.

2. *Ammonia.*—3000 grs. of the mineral water were introduced into an appropriate tubulated glass retort, and mixed with half an ounce of caustic soda. The vapours were, during distillation, conducted under dilute hydrochloric acid, and the operation finished, when only 2 ounces were left in the retort. The distilled fluid previously mixed with chloride of platinum was evaporated in a porcelain vessel. [I have to notice, that without this addition of the chloride of platinum no correct results can be obtained, even at a temperature below 212° Fahr., inasmuch as the chloride of ammonium rises with the aqueous vapours. This is easily ascertained by covering the vessel during evaporation with filtering paper, which when lixiviated will clearly evidence the presence of chloride of ammonium, a circumstance which Berzelius has already noticed in his Manual of Chemistry, vol. x.] The dry residue was lixiviated by a mixture of 2 volumes of alcohol and 1 volume of æther, in which mixture the ammonio-chloride of platinum is perfectly insoluble. The edulcoration was carried on until all acid reaction upon litmus paper ceased, when the precipi-

* An amount which comes near to 84·301 grs., but of course free from organic matter, which the latter amount includes.

tate was dried at 212° Fahr. and weighed 15·406 grs. To control the correctness of the weight, the precipitate and filter were placed in a platina crucible, and ignited in the manner described by H. Rose in his Analytical Manual, when 6·8138 grs. of platina were obtained, which corresponds with the amount of platina derived by calculation from 15·406 grs., viz. 6·8142 grs. The amount of ammonia calculated from these data for 16 ounces is 3·033 grs.

If we now arrange the electro-negative and electro-positive ingredients, thus established, into binary combinations in the ratio of their mutual affinities, it will be found that there is a surplus of bases, one of which must obviously be united to the organic matter; and I am inclined to think that a combination of ammonia and organic matter has existed. I regret that the small quantity of water (12 wine bottles) obtained for analysis from Scotland did not permit me to study the nature of the organic matter, but there is no doubt that it belonged to the group of decaying substances. The few experiments I was enabled to perform evidenced the absence of crenic and apocrenic acid, namely, when the water was evaporated to one-tenth of its volume, neutralized by acetic acid, and mixed with acetate of copper and heated, no indication of these acids was perceptible. Acetate of lead gave a precipitate; it did not however separate the organic matter entirely. That the source of ammonia stands in intimate connection with that of the organic matter admits scarcely of doubt, particularly since Mulder* and R. Herrman of Moscow have established that some of the class of humus acids contain ammonia. If mouldering wood, garden-earth, &c. are extracted by alcohol and then with water, and the residue treated with alkalies, a humus acid is obtained, which, besides carbon and the elements of water, contains a certain proportion of ammonia in chemical combination. By the analysis of such an acid derived from the soil of a meadow, the following results were obtained, expressed in this formula:—

$$2\,N_2\,H_6\,OH_2 + C_{40}\,H_{28}\,O_{14}.$$

Mulder's analyses prove also that in a fertile soil combinanations of ammonia with those acids exist, derived from the decay of vegetable matter; but these acids correspond with humus acid, inasmuch as they have the same number of equivalents of carbon (40), but vary in the proportion of oxygen and hydrogen. It is obvious from the foregoing results, that mineral waters containing alkalies, when they come in contact with strata interspersed with humus, must become partly im-

* See Berzelius's *Jahresbericht*, 21st Jahrgang, 3rd Heft.

pregnated with ammonia and these organic acids, produced by the decay of vegetable matter.

The result of the analysis gives the following binary combinations in 16 oz. troy of the water:—

	Anhydrous ingredients.	In 1000 grs.
Sulphate of potassa	2·15838	0·28104
... soda	1·32389	0·17238
... lime	5·49913	0·71603
Iodide of sodium	0·00637	0·00083
Bromide of sodium	0·06900	0·00899
Chloride of ammonium . . .	8·31609	1·08281
... sodium	3·35254	0·43653
... magnesium . . .	2·73148	0·35566
Nitrate of soda	1·76972	0·23043
Carbonate of magnesia . . .	1·49118	0·19417
Proto-carbonate of iron . . .	0·05080	0·00662
... ... manganese .	0·01343	0·00175
Ammonia (united to organic matter)	0·37017	0·04820
Alumina	0·01970	0·00256
Silica	0·16330	0·02126
Total in grs. .	27·33518	3·55926

If the total amount calculated upon 1000 grs., namely, 3·559 grs. is compared with that obtained by the evaporation of 1000 grs.—3·712 grs.—we find a deficiency of 0·153 gr., which belongs to the organic matter; yet it is to be observed, that the amount 3·712 cannot be very exact, as during evaporation a small proportion of ammonia must have been dissipated. To prove if the results of the analysis of the fixed bases are correct, they were computed to sulphates and compared with the result obtained by evaporating 1000 grs. of the water, igniting the residue to a red heat, and mixing it with a due quantity of sulphuric acid, and again igniting it until the surplus of sulphuric acid was dissipated, when it yielded 2·663 grs.

Changing in this way the fixed ingredients into sulphates, by computation we have—

	grs.
Sulphate of potassa	2·158
... soda	6·930
... lime	5·499
... magnesia	5·569
... alumina	0·065
Proto-sulphate of iron	0·067
... ... manganese . .	0·021
Silica	0·163
Total . . .	20·472

This amount gives upon 1000 grs. 2·665, a result very close indeed to 2·663, as obtained by experiment, where the iron, manganese and alumina might have lost during ignition a small quantity of sulphuric acid.

A few small flakes, which were found floating in the water, and which were separated, remain finally to be noticed. These flakes consisted chiefly of oxide of iron with a small proportion of organic matter. The oxide of iron upon 16 ozs. amounted to 0·384 gr., which had become separated (as I was assured) from the water in the bottles, and must have existed previously in the form of a proto-carbonate of iron, which would be equivalent to the amount of 0·56175. On adding this to the iron found in solution, 16 troy oz. of the water would contain at its source 0·61255 gr. of proto-carbonate of iron, or in 1000 grs. 0·07975 gr.

For convenience sake the calculation upon the imperial pint is added.

In 1 pint = 34·659 cubic inches (at 60° F. spec. grav. 1·002618) = 8772·907 grs.

	grs.
Sulphate of potassa	2·46554
... soda	1·51227
... lime	6·28166
Iodide of sodium	0·00728
Bromide of sodium	0·07886
Chloride of ammonium	9·49939
... sodium	3·82963
... magnesium	3·12017
Nitrate of soda	2·02154
Carbonate of magnesia	1·70443
Proto-carbonate of iron	0·05807
... ... manganese	0·01535
Ammonia (united to organic matter)	0·42285
Alumina	0·02245
Silica	0·18651
Total	31·22600

The whole amount of proto-carbonate of iron in 1 pint at the source = 0·69973 gr.

CXVII. *Description of a Chemical Lamp-Furnace.* *By* Edward Solly, *Esq.*

At the meeting of the British Association last September in York, the Rev. W. Vernon Harcourt exhibited a hydrogen lamp-furnace, the object of which was to afford a

steady, uniform heat to a platinum vessel, sufficiently high to effect the ready fusion of vitreous substances by means of a fuel, free from those objections attending the use of one containing solid carbonaceous matter. Mr. Harcourt's furnace consisted of a number of jets arranged round the crucible to be heated, which, to ensure uniformity of temperature, was suspended by three platinum wires from a watch movement, which caused it to rotate slowly on its vertical axis; the fuel employed was hydrogen, generated in a strong iron reservoir, and burnt under a pressure of from 10 to 30 atmospheres. The mechanical arrangements of this lamp-furnace were very beautiful, and the heat produced by the combustion of the jets of compressed hydrogen directed against the bottom and sides of the revolving crucible was steady, intense, and apparently manageable; but the instrument was of course very expensive, and required considerable care in its use.

The exhibition of this apparatus suggested to me the possibility of constructing a lamp on a similar principle, but far less expensive, and sufficiently simple for ordinary use; which, though it might not afford so high or pure a source of heat as the arrangement of Mr. Harcourt, might yet constitute a useful instrument in the laboratory: as, on trial, I found my plan perfectly successful, I am led to think that a brief description of the lamp will be interesting to others.

It is well known that when coal-gas is mixed with a certain proportion of air it burns with a pale blue flame containing no solid carbon, and therefore giving only a very feeble light, but possessing a very high temperature, so much so, that the large pale flame of gas mixed with air and burnt above a diaphragm of wire gauze is very commonly employed when a higher temperature is required than can be obtained by the mere use of an Argand lamp. It appeared probable, after seeing Mr. Harcourt's lamp, that a very high temperature might be obtained by burning a mixture of air and coal-gas, in place of hydrogen, in a suitable arrangement of jets. The form of lamp which, after a few trials, I found best adapted for this purpose, consists of two circles of jets, one vertical and the other horizontal, the latter being raised nearly two inches higher than the former. The vertical circle consists of a metal ring, about an inch in diameter, pierced on its upper side by six small holes or jets; the horizontal circle consists of a hollow metal ring, having an internal diameter of rather more than three inches, with twelve holes drilled on its inner side, so as to form altogether a series of eighteen little jets of flame, six vertical and twelve horizontal, all converging to a common centre, which is of course the point of

the greatest heat. The mixture of coal-gas and air burnt in this lamp, is made by injecting a sufficient quantity of air into the pipe which supplies the coal-gas. To the end of a common gas-cock connected with the street main, a piece of copper pipe about four inches long is attached, having a diameter of about a quarter of an inch; outside this is another piece of copper tube, of considerably larger diameter, and six inches longer than the internal tube. The air which is to mix with the coal-gas is admitted into this longer external tube, the quantity being regulated by cocks. The object of this is to effect the mixture of the air and coal-gas under the most favourable circumstances; if mixed otherwise than as two currents flowing in the same direction, a diminution of pressure is caused; whilst by causing them to mix in the manner just described, the pressure of the whole current is rather augmented.

The pressure of the ordinary street gas does not, I believe, generally exceed two inches; if the air was introduced by a pipe entering the gas-pipe at right angles, and if the pressure of the air at all exceeded that of the gas, it was very apt to stop the current of gas altogether, the air forcing the gas back into the pipe; by using the above double pipe this was obviated, and it was found possible slightly to increase the pressure of the air over that of the gas without at all diminishing its force. At first a gasometer was employed as a source of air, but after a few trials it was found that a common double bellows was more convenient; when the lamp is used, the crucible to be heated is supported on the top of the horizontal circle of jets by a triangle of platinum wire, so as to place it in the centre of greatest heat. If only the gas is lighted, it of course burns with a large and very smoky flame, depositing abundance of solid carbon; but the moment the air is admitted, the flame begins to diminish in size and also in brilliancy, burning, when a sufficient proportion of air is allowed to enter, with a pale blue colour, and perfectly free from solid carbon. The crucible is, in fact, heated by eighteen little blowpipes, and of course becomes brightly ignited in a few seconds, the heat continuing to increase as the ignited platinum facilitates the more complete combustion of the gas and air, causing the blue flame of each jet to be edged with pale yellow, and considerably increasing them in size; lastly, the furnace is rendered complete by a thin cylinder of sheet iron, three inches in diameter and two high, which is placed above the horizontal circle to prevent the flames being blown about by draught of air, and a circular disc of the same metal, having a hole in its centre of an inch across, to place at the top of the cylinder:

this causes the heated air to pass round the upper edges and over the lid of the crucible, so as to bring the whole to the same temperature.

With this arrangement it is easy to keep a platinum crucible two inches high and an inch and a half across at a bright red or yellow heat for any required time; the heat is perfectly manageable, the gas may be turned off at any moment, and as quickly lighted; hence any operation is far more under control than in a furnace. The heat obtained with a crucible of the size just mentioned is rather above the melting-point of silver, for a piece of that metal is easily fused in a porcelain crucible placed in the interior of the platinum one. It is of course equal to the fusion of mixtures of silicates with carbonate of soda, three or four hundred grains of a mixture of carbonate of soda and a siliceous compound being perfectly fused in about eight minutes, whilst from the entire command at all times had over the source of heat, it is easy to moderate it when the evolution of carbonic acid is too rapid, and to stop it as soon as the operation is complete; in fact, the progress of the experiment may be watched from the commencement to the end with the greatest facility.

The object which I had originally in view in the construction of this lamp, was to obtain a cheap, simple and efficacious method of heating a platinum crucible to bright redness without exposing it to the contact of solid fuel, and in this the attempt was perfectly successful. The decomposition of earthy silicates may, it is true, be very easily effected in an ordinary furnace; the crucible being protected from contact with the fuel by placing it in an earthen one, or by wrapping it in a thin piece of platinum foil, which preserves the crucible very perfectly from the action of the fuel in a cheap and very convenient method; but still, the above lamp-furnace is decidedly superior to that or indeed any other mode I have tried. Independent even of the question of œconomy, I prefer it to the Argand spirit-lamp.

As the use of such a lamp must in part depend on its simplicity, I was anxious not to complicate it more than was absolutely necessary; but I have no doubt that its power might be very greatly augmented; in its present state, however, it is useful for several purposes besides the mere ignition of a crucible, such as, for example, glass-blowing and bending large or thick tubes; in fact, in all cases where a bright red or yellow heat is required, and where an ordinary furnace is inapplicable.

CXVIII. *Notice of a new Hydrated Phosphate of Lime.* By John Percy, *M.D.*

TO a solution of common phosphate of soda, in a *large* quantity of distilled water, add a solution of chloride of calcium till precipitation ceases. Immediately pass through the mixture, containing the phosphate of lime suspended, a current of carbonic acid gas, and continue this for about an hour; then filter immediately, and set aside the filtered liquor in a jar, the mouth of which is covered loosely with paper to keep out dust. In the course of a day or two, and sometimes in a much shorter time, crystals will appear on the surface, and will, when stirred with a rod, sink. After the lapse of several days a very sensible quantity of crystals may be collected. Transfer them to a filter, and wash with cold or tepid distilled water, and dry in a *warm* place.

It occurs in the form of brilliant white scales, which, on examination with the microscope, are seen to consist of modified rhomboidal plates more or less broken and confused.

The salt melts with difficulty at an intense heat by the blowpipe on platinum foil. Heated to bright redness in a platinum crucible, 3·21 grs. of salt lost 0·85, and in a second experiment 3·16 grs. lost 0·84 gr. I found that every trace of water was given off after exposure for 10 minutes or a quarter of an hour to a bright red heat.

Rose's plan was followed in determining the lime and phosphoric acid, which consists in dissolving in hydrochloric acid, then adding sulphuric acid, then alcohol, which precipitates the lime completely as sulphate.

I. 3·21 grs. of salt gave 2·51 of sulphate of lime.
II. 3·16 grs. ... 2·48 ... ...

Taking 28 as the equivalent of lime, and phosphoric acid as 72, we have—

	First analysis.	Second analysis.
Water	0·85	0·84
Lime	1·04	1·02
Phosphoric acid . .	1·32	1·30
	3·21	3·16

The oxygen of the water is three times as much as that of the base, and the salt agrees in composition with the formula

$$2CaO + PO_5 + 6HO.$$

The rational formula will, doubtless, be HO, 2CaO, PO_5 + 5HO, 1 equiv. of water being basic and 5 constitutional.

2·40 grs. of this phosphate heated in the oil-bath at a temperature between 134° and 148° centig., lost 0·30 gr. in $1\frac{1}{2}$ hour, and no more than 0·31 gr. in $4\frac{3}{4}$ hours, while at a red heat it would lose 0·60 gr. 0·60 − 0·31 = 0·29. We may

therefore conclude that one-half of the water is expelled at the temperature above mentioned, giving another hydrate, HO, $2CaO + PO_5 + 2HO$.

CXIX. *On a curious Change in the Composition of Bones taken from the Guano.* By Robert Warington, *Esq.*

MY friend Mr. Edwin Quekett, put into my hands a few days since, for the purpose of chemical examination, a curious crystalline substance taken from the guano, as imported from Ichaboe, and which he considered to have entirely replaced, and thus have assumed the form of, the original bony structure. The exterior surface, in many specimens, has portions of muscular fibre in a dry and pulverulent state closely in contact with the substance; small pieces of bony matter are also now and then found remaining, and in some cases the cylindrical part of the bone is perfectly modelled by this saline deposition or infiltration. The structure is highly crystalline and laminated, and in the cylindrical parts slightly radiating from the sides towards the centre; its colour is nearly white, with a slight shade of yellow, and generally very free from foreign matter, except at the parts where the enlarged or natural terminations of the bones may be supposed to have been, and in these places the substance is interspersed with small brown particles. It decrepitates in the flame of the spirit-lamp, assumes a gray colour, gives off ammoniacal vapour, and ultimately becomes perfectly white and opake; and by increasing the heat, by means of the blowpipe, it fuses and communicates a pinkish purple tinge to the flame, indicative of potash, and without any trace of yellow, showing its perfect freedom from soda salts. It was readily dissolved in hot distilled water, with the exception of the interspersed brown particles just alluded to; solution of nitrate of barytes threw down an abundant white granular precipitate insoluble in dilute nitric acid, consequently proving the presence, to a considerable extent, of sulphuric acid; solution of chloride of calcium occasioned no change, nor did the subsequent addition of ammonia cause any precipitation, so that the oxalic and phosphoric acids were both absent. Solution of oxalate of ammonia gave no indication of the presence of lime. By boiling, after adding solution of caustic potash, ammonia was evolved; nitrate of silver in a dilute solution, free nitric acid being present, caused no precipitation. The addition of tartaric acid in excess caused the rapid and plentiful separation of bitartrate of potash; and on evaporating a little of the solution of this substance, to which a few drops of nitric acid had been added, to dryness, a small quantity of uric acid was

evidenced by the production of the crimson stain so peculiar to that compound; magnesia was also tested for but was not detected.

It is evident from this qualitative examination that this substance was composed, for the most part, of sulphuric acid, potash and ammonia, with a little uric acid. The following quantitative analyses were therefore undertaken:—5·84 grs. of the whitest and cleanest part were selected and heated to redness in a closed platinum crucible for some time, it lost 1·02 gr., leaving a perfectly white and opake residue, without much alteration of the original form of the fragments. During this operation a slight quantity of acid vapour was given off. This residue was boiled in distilled water, which dissolved nearly the whole, with the exception of a few particles weighing 0·06 gr., having an opake white colour, similar to the bulk of the residue, and which proved on examination to be the bone-earth phosphate of lime; they were slowly dissolved in dilute nitric acid without any appearance of effervescence, and gave indications of the presence of phosphoric acid and lime, the first by solution of nitrate of silver, and by a solution of the ammonio-chloride of magnesium, the latter by oxalate of ammonia. We have, therefore,

4·76 grs.		fixed residue assumed to be sulphate of potash.
0·06	...	bone-earth phosphate of lime.
1·02	...	loss by heat, assumed to be sulphate of ammonia and water.
5·84		

14·54 grs. of the substance were digested with boiling distilled water, and the undissolved portion (*a*) collected on a filter; it weighed 1·44 gr., and consisted entirely of the muscular fibres and the brown particles previously mentioned. The solution was then divided accurately into two equal parts, to one of which a little nitric acid was added, heated to the boiling-point and precipitated by a solution of nitrate of barytes as long as any sulphate of barytes was thrown down; it was then collected, washed, ignited, and gave 8·8 grs. of sulphate of barytes, equal to 3·00 grs. sulphuric acid (*b*); this precipitate was accompanied by a very small quantity of a flocculent matter of a pale brown colour. The excess of barytes was next separated by the addition of sulphuric acid, and the filtrate evaporated to dryness, when the crimson stain, denoting the existence of uric acid, was evident; on re-solution in water a pale brown flocculent matter separated (*c*), similar to what had been just noticed; this was separated by a filter and weighed 0·11 gr.; the solution was then evaporated to dryness and heated to expel the excess of sulphuric acid which had

been added; the residue (*d*) of bi-sulphate of potash weighed 7·85 grs., equivalent to 2·94 grs. of potash. The second half of the solution was treated with caustic potash and submitted to distillation until reduced to a very small volume, the volatile products being passed into dilute hydrochloric acid; to this a solution of chloride of platinum was added, and the whole evaporated to dryness and then re-dissolved in a mixture of alcohol and æther, which left 3·44 grs. of ammonio-chloride of platinum, equivalent to ·26 gr. of ammonia (*e*).

We have, therefore, from this analysis, the following results:—

Sulphuric acid (*b*)	3·00 grs.	× 2 =	6·00 grs.
Potash (*d*) . . .	2·94 ...	× 2 =	5·88 ...
Ammonia (*e*) . .	0·26 ...	× 2 =	0·52 ...
Flocculent matter (*c*)	0·11 ...	× 2 =	0·22 ...
Insoluble (*a*) . .			1·44 ...

If we now arrange the bases with the acid to form salts, we shall have—

Potash . . .	5·88 grs.	= 10·78 grs. sulph. of potash.
Sulphuric acid .	4·90 ...	
Ammonia . . .	0·52 ...	= 2·29 ... sulph. of ammonia.
Sulphuric acid .	1·22 ...	
Water of crystallization . . .	0·55 ...	

There is, however, a deficiency in the experimental quantity of sulphuric acid amounting to 0·12 gr., as will be seen on comparing this arrangement with the analytical results. These two salts appear to be associated in this substance in atomic proportions, thus:—

		Theory.	Experiment.
Sulphate of potash	4 eqs.	= 10·8	10·78
Sulphate of ammonia	1 eq.	= 2·3	2·29

It will be evident from the above examination, that this substance is not perfectly constant in its composition; for in the first quantitative analysis a small quantity of phosphate of lime was present, which did not exist in the portion which formed the subject of the second analysis, nor in that of the qualitative examination.

The curious question which arises from these investigations, is as to the probable source of the sulphate of potash in a substance taken from the midst of a material, the guano, abounding in soda and ammoniacal salts, and for the moment this appears to baffle our present information on the localities of these deposits. I have been lately thrown into a train of communication from which I have gained some curious information, which may, to a certain extent, assist in elucidating the point. It appears that the seal-fishers have for a long series

of years been in the constant habit of frequenting this island, Ichaboe, as a convenient spot for the purpose of extracting the oil from the fat of the seals which they may have caught; and this is effected by melting the fat over a wood fire, the fuel for the purpose being collected on the island, the carcases of the seals being thrown aside as useless, and becoming the food of the innumerable sea birds frequenting the district, and thus giving rise to the deposit of the guano on, or in close proximity to, the spot where the ashes of the wood fires and the bodies of the seals had been left; and hence we may, to a certain extent, argue on the source of the potash and its decomposing the ammoniacal salts existent in the putrefying carcases or the deposit of the birds. It will also account for the frequent occurrence of the skin and bones of the seal as observed in much of the imported guano.

December 2, 1844.—Robert Porrett, Esq., Treasurer, in the Chair.

"Account of a repetition of several of Dr. Brown's processes for the Conversion of Carbon into Silicon," by George Wilson, M.D. and John C. Brown, Esq., was presented from the authors.

John Percy, M.D., and William Papineau, Esq., were elected Members of the Society.

The following communications were then read:—

CXX. *On a means of detecting Kinic Acid.*

By John Stenhouse, *Ph.D.*

THOUGH kinic acid does not possess any very striking characters by which it can be easily recognised, its presence may be readily collected by converting it into that very remarkable product of its decomposition, kinone. As there is good reason for believing that kinic acid exists in the state of kinate of lime in all the barks which contain the alkaloids quinine and cinchonine, it may perhaps be of some importance to describe an easy mode of detecting kinic acid, as this may facilitate the discrimination of the true cinchona barks from the spurious ones.

To examine a bark for kinic acid, it is merely necessary to boil a little of it, say a quarter of an ounce, with a slight excess of lime. The liquor may be poured off and concentrated, as it is not necessary to filter it. It is then to be introduced into a retort and distilled with a mixture of half its weight of sulphuric acid and peroxide of manganese. If the bark contains the smallest quantity of kinic acid, the first portion of the liquid which distils over has a yellow colour and the very peculiar smell of kinone. If the liquid is treated with a little ammonia, it immediately becomes of a deep brown colour, which in a few minutes changes to brownish black; or if a little chlorine water is added to a second portion of the liquid,

it changes from a yellow to a bright green colour. The distillation need not be long continued, as the kinone is very volatile, and comes nearly all over at the first. I have tried this experiment with the genuine barks *China rubra*, *China loxa*, and *China regia*, and detected the kinic acid very readily, when less than a quarter of an ounce of each was employed. I have also operated on two ounces of the false bark, *China nova Surinamensis*, but was unable to detect the least trace of kinic acid.

It has long been stated in most systems of chemistry, on the authority of Berzelius, that the alburnum of *Pinus sylvestris* contains a half per cent. of kinate of lime, and that kinic acid exists along with gallic acid in the barks of various other trees. A pound and a half of the inner bark and alburnum of the *Pinus sylvestris* was treated in the way already described, but I was unable to detect any trace of kinic acid; though on adding less than two grains of kinate of lime the presence of kinone in the liquid which distilled over was immediately perceptible.

I may state, in conclusion, that the presence of the vegetable alkaloids quinine or cinchonine in a bark may be readily detected by the following simple experiment. Macerate the bark with dilute sulphuric acid and precipitate with a slight excess of carbonate of soda or potash. Collect the dark-coloured, very impure precipitate, and distil it with a great excess of caustic soda or potash, cincholin will distil over in oily drops if the bark has contained either of these vegetable alkaloids. Cincholin is easily recognisable by its peculiar taste and smell and its strongly-marked alkaline properties. It is nearly insoluble in water, unless first neutralized by an acid, when it readily dissolves; but it is immediately reprecipitated in oily drops on the addition of an alkali. It is quite true that the production of cincholin is not a decisive proof that a bark must necessarily contain quinine or cinchonine, as other alkaloids, such for instance as strychnine, also yield it when distilled with potash. The production of cincholin, however, clearly indicates the existence of at least one alkaloid in the bark, the exact nature of which may be subsequently ascertained by the usual methods.

CXXI. *Remarks upon Chloranil.* By Augustus William Hofmann, *Ph.D.*

Erdmann*, in his researches upon the action of chlorine on indigo, obtained, as the last product of this reaction, a crystalline body free from hydrogen, to which he gave the

* *Journ. fur Prakt. Chem.*, Bd. xxii. S. 279.

name chloranil. This substance, remarkable on account of the series of interesting transformations which it undergoes when in contact with the alkalies, has been diligently studied by Erdmann. From his experiments, the composition of chloranil is represented by the formula—

$$C_6\,Cl_2\,O_2.$$

This body has lately become the starting-point of some interesting discussions, which Laurent* brought before the Academy at Paris. The view of this chemist assumes the equivalent of chloranil to be double, agreeing with the formula,—

$$C_{12}\,Cl_4\,O_4.$$

The method which Erdmann employed for obtaining chloranil is circuitous, and yields very little of that substance. He passed a stream of chlorine gas through an alcoholic solution of chlorisatin or bichlorisatin. The following equation represents the transformation of the chlorisatin into chloranil:—

$$\underbrace{C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}NO_4}_{\text{Chlorisatin.}} + 8O + 4Cl = \underbrace{C_{12}Cl_4O_4}_{\text{Chloranil.}} + 4CO_2 + NH_3 + HCl.$$

The process is not, however, so simple, as there is formed at the same time chlorinated chlorindoptic acid (Laurent's chlorophenussic acid†), as well as many other secondary products, and there is obtained a comparatively small quantity only of chloranil.

Somewhat later chloranil was re-observed under other circumstances. Fritzsche‡ found, in some experiments upon the blue colour assumed by anilene from the action of the oxygen compounds of chlorine, that by a continued digestion of a mixture of chlorate of potash and hydrochloric acid upon anilene, chloranil is also formed.

I have had the opportunity, in a research upon the organic bases of coal-gas naphtha§, to confirm this statement; the whole of the carbon of the anilene enters into the chloranil, as the following equation shows:—

$$\underbrace{C_{12}H_7N}_{\text{Anilene.}}, 4O + 8Cl = \underbrace{C_{12}H_4O_4}_{\text{Chloranil.}} + NH_3 + 4HCl.$$

The close relation subsisting between the anilene and phenyle series induced me to try whether chloranil could not be obtained from different members of this group of bodies. I soon learnt that chloranil is often formed, as the last product of decomposition of organic bodies, under the

* *Comptes Rendus*, t. xix. No. 6. S. 316.
† *Ann. de Chem. et de Phys.*, 3me ser. t. iii. p. 498.
‡ *Bullet. Scient. de St. Pétersb.*, 1843, t. i. p. 103.
§ Philosophical Magazine, Third Series, vol. xxiv. p. 199.

united influence of oxygen and chlorine. I commenced my investigation with the hydrate of phenyle, and selected as a means of oxidation a mixture of hydrochloric acid and chlorate of potash, in which oxygen and chlorine are disposable. When hydrate of phenyle in a porcelain basin is treated with strong hydrochloric acid, and there is added at intervals small crystals of chlorate of potash, a violent reaction ensues, and the colourless oil acquires a reddish-brown colour and inspissates. If the action has lasted sufficiently long, the whole mass changes to a light yellow crystalline matter, which is no other than chloranil. As it takes a long time to ensure perfect decomposition, it is advisable towards the end of the process to apply heat, in order to promote the action. I have endeavoured to shorten the time by employing an alcoholic solution of hydrate of phenyle; the decomposition then takes place indeed quicker, but a great quantity of chlorate of potash is wasted by the conversion of the alcohol into acetic æther. When alcohol is used, the addition of strong hydrochloric acid, or too quick an introduction of large quantities of chlorate of potash must be avoided, as the mass inflames readily with explosion. These explosions even sometimes take place when no alcohol has been added; it is therefore always advantageous to conduct the operation in basins.

If a boiling saturated aqueous solution of hydrate of phenyle is employed it saves time, and also chlorate of potash; or a watery extract of coal-gas naphtha may be at once taken, as it contains anilene and hydrate of phenyle, both being convertible into chloranil. The produce is in this way, however, very limited, owing to the slight solubility of these two compounds in water*.

To purify the chloranil it is only necessary to affuse with water, which dissolves any adhering chloride of potassium, and to crystallize from alcohol. This menstruum dissolves the chloranil with difficulty in the heat; and on cooling the whole deposits.

I have compared minutely the properties of the substance obtained in this way with those given by Erdmann in his treatise on chloranil, and find that they agree perfectly. The body I procured from hydrate of phenyle, as was before remarked, is insoluble in water, dissolved with difficulty by alcohol, but more easily by æther, and crystallizes from the two latter solvents in shining golden-yellow plates; the mother-liquor assumes a violet tint when exposed to the air. It begins

* In an experiment where I treated the coal-gas naphtha with the oxidizing mixture there was no chloranil found, apparently owing to its quantity being so minute when compared with that of the other products.

to volatilize at 302° F., and between 410–428° F. the sublimation is rapid; if it be heated above this temperature it melts, and is finally carbonized. The sublimate has the appearance of an extremely soft, light, iridescent powder, which remains intact with acids, but when treated with alkalies is changed with the greatest facility. When the crystals are drenched with a dilute potash-ley, they acquire immediately a dark colour with a shade of green, but on the application of heat dissolve to a blood-red fluid, from which purple needles of an organic salt are deposited upon cooling. These needles, when immersed in dilute hydrochloric acid, assume, without altering their form, a bright red colour. They are quite insoluble in very dilute acids, but dissolve in pure water with a beautiful violet hue. By the addition of hydrochloric acid the liquid is discoloured immediately, and after some time the red crystals again deposit.

There can be no doubt from the foregoing that the substance obtained from the hydrate of phenyle and Erdmann's chloranil are identical. I have notwithstanding made some combustions of this compound. The analyses were however made with a product which was only recrystallized from alcohol, and not sublimed; the substance was therefore not quite pure, a circumstance which Erdmann had found previously. In five analyses this chemist always obtained a constant excess of carbon: my analyses were also encumbered with the same fault, owing to which there is a discrepancy between the chlorine found and that of theory.

I. 0·5845 grm. of substance ignited with chromate of lead, gave 0·6474 grm. of carbonic acid and 0·0212 grm. water.

II. 0·4615 grm. of substance ignited with chromate of lead, gave 0·5090 grm. of carbonic acid and 0·0120 grm. water.

III. 0·2555 grm. of substance ignited with lime and dissolved in nitric acid, gave 0·5820 grm. of chloride of silver.

These numbers, represented in the 100 parts, give,—

	I.	II.	III.
Carbon .	30·20	30·07	
Hydrogen	0·40	0·28	
Chlorine .	.....	.....	56·20

Erdmann found as a mean of five combustions of the chloranil crystallized from alcohol, 30·20 per cent. carbon *. The following is the theoretical composition of the chloranil:—

12 equivs. Carbon . .	900·00	29·33
4 equivs. Chlorine . .	1770·60	57·66
4 equivs. Oxygen . .	400·00	13·01
	3070·60	100·00

* Carbon taken at 75.

If the formulæ of hydrate of phenyle and chloranil be compared, the transit of the one into the other is at once perceived.

$$\underbrace{C_{12}\,H_6\,O_2}_{\text{Hydrate of phenyle.}}+2O+10Cl=\underbrace{C_{12}\,Cl_4\,O_4}_{\text{Chloranil.}}+6H\,Cl.$$

The foregoing equation gives the final result of the decomposition; but I must remark that another compound precedes the formation of the chloranil. If the process be interrupted when the hydrate of phenyle becomes somewhat glutinous, a solid crystalline mass will result upon cooling, in which the chloranil is enveloped by a red, tenacious, disagreeably-smelling resin, dissolving in every proportion in alcohol, and this property allows of its easy separation from the former. When the alcoholic solution of the resinous mass is submitted to distillation, what remains in the retort becomes fluid as soon as the spirit has passed off, and along with the abundant disengagement of hydrochloric acid there distils over a heavy red oil, which sometimes solidifies in the receiver, charcoal remaining in the retort.

The distillate obtained in this way dissolves in potash or ammonia. Such a solution not containing an excess of the alkali, gives with copper and silver salts the purple, violet and yellow precipitates, characteristic of chlorophenissic and chlorophenussic acids.

The circumstances under which the acid had formed made it probable that it was chlorinated chlorindoptic acid (chlorophenussic acid), particularly as it appeared collaterally with chloranil in the method originally followed by Erdmann. It might however have been chlorophenissic, or else a mixture of the two acids.

To solve this question, I decomposed the filtered potash compound of the distillate with sulphuric acid, and obtained a feebly-coloured precipitate, which was collected on a filter, edulcorated, desiccated, and in order to remove the last traces of water, fused at a low temperature. By the distillation of this dry mass, a thick colourless oil condensed in the receiver, and also in the lower portion of the neck of the retort, which became a solid mass of a crystalline structure, possessing, with the exception of the odour, the greatest resemblance to stearic acid.

Determination of the chlorine in this compound:—

0·5229 grm. of substance ignited with lime, &c., gave 1·1334 grm. of chloride of silver = 53·47 per cent. chlorine.

The preceding analysis shows the compound to be chlorophenissic acid $C_{12}\,\overset{H_2}{Cl_3}\,O+HO=53{\cdot}51$ per ct. chlorine, while

the chlorophenussic acid $C_{12}Cl_5O + HO = 66{\cdot}50$ per ct. chlorine.

In this way a large quantity of chlorophenissic acid may be readily obtained as an accompanying product in the preparation of chloranil.

From the foregoing it is seen that the chlorophenissic acid can be transformed into chloranil, of which fact I have also convinced myself by direct experiment. It occurred to me to endeavour to produce chloranil from other members of the phenyle series. By a longer or shorter action of nitric acid upon hydrate of phenyle, Laurent converted it into nitrophenessic and nitrophenissic acids (carbazotic acid). These two acids, when treated with hydrochloric acid and chlorate of potash, yield chloranil with the greatest facility. When nitrophenessic acid is taken, alcohol should be employed, on account of its insolubility in water.

Schunck* obtained some years ago, in treating aloes with nitric acid, an acid (chrysolepinic) having the same composition and the greatest similarity with carbazotic acid, but which was said to be different on account of some deviations in its compounds. It was therefore the more interesting to produce chloranil from this body, as Marchand† has asserted lately that the carbazotic and the chrysolepinic acids are identical. The chrysolepinic acid is indeed transformed into chloranil. I have repeated this experiment several times with complete success, as well with a product which I prepared as with a specimen which Schunck had left in the collection of Professor Liebig.

The new researches of Gerhardt‡ and Cahours§ have shown so close a connection between the compounds of phenyle and those of salicyle, that the conversion of the latter into chloranil was to be expected. To produce this metamorphosis, it is indeed only necessary to boil salicylous acid (salicide of hydrogen), salicylic acid, or nitrosalicylic acid (indigotic or anilic acid), with hydrochloric acid and chlorate of potash. The decomposition in all these cases is very simple, the superfluous carbon escaping in the form of carbonic acid, *e. g.*

$$\underbrace{C_{14}H_5O_3 + HO}_{\text{Salicylous acid.}} + 10Cl + 4O = \underbrace{C_{12}Cl_4O_4}_{\text{Chloranil.}} + 2CO_2 + 6HCl.$$

Although it is known that benzoic acid and salicylous acid are identical, still the former, when treated as above, does not

* Liebig's *Ann.*, Bd. xxxix. S. 7.
† *Journ. für Prakt. Chem.*, Bd. xxxii. S. 35.
‡ Liebig's *Ann.*, Bd. xlv. S. 19.
§ *Ann. de Chim. et de Phys.*, 3me S. t. x. p. 327.

yield chloranil. This is the case also with nitrobenzoic acid, benzine, nitrobenzide, binitrobenzide, and hydruret of benzyle (oil of bitter almonds).

It yet remained to try the preparation of chloranil from salicine, the basis of all the salicyle compounds, when indeed the anticipated transformation occurred. This decomposition is readily comprehended, if it be remembered that the salicine contains the elements of 3 eqs. of salicylous acid and 10 eqs. of water, *e. g.*

$$\underbrace{C_{42}H_{28}O_{22}}_{\text{Salicine.}} + 24Cl + 18O = 3\underbrace{(C_{12}Cl_4O_4)}_{\text{Chloranil.}} + 6CO_2 + 16HO + 12HCl.$$

The salicine is, on account of its solubility in water, perhaps the fittest substance for yielding large quantities of chloranil. It is only requisite to dissolve salicine and chlorate of potash in boiling water and to add at intervals small quantities of hydrochloric acid. By degrees the mixture assumes a deep orange yellow colour, which is followed by a violent reaction; and besides the products of decomposition resulting from the chloric acid, there escapes a large portion of carbonic acid, and the surface of the liquid becomes covered with a thick layer of sulphur-yellow crystals of chloranil.

The salicine must not be treated with hydrochloric acid and then the crystals of chlorate of potash added, for the acid will transform the salicine into salicetine, which cannot be resolved into chloranil. Even by a long-continued boiling of the salicetine with the oxidizing mixture, nothing is obtained but a yellow uncrystalline mass insoluble in water and alcohol. I have made a burning of the chloranil procured from salicine and obtained the following numbers:—

0·373 grm. of chloranil gave 0·414 grm. of carbonic acid = 30·27 per cent.

Neither phloridzine, phloretine, cumarin, nor cinnamic acid, are transformable into chloranil. The first three furnish, by the action of chlorate of potash, yellow resinous bodies insoluble in water but soluble in alcohol, while the last is converted into a colourless oil, to which I shall recur in a future paper. It is almost superfluous to remark, that if chloranil is prepared from isatine, chlorisatine or bichlorisatine, the transformation takes place quicker and more completely by the employment of a mixture of hydrochloric acid and chlorate of potash than by conducting a stream of chlorine through the alcoholic solution, for in a few minutes the conversion of considerable quantities is effected. Anthanilic acid also naturally suffers the same decomposition.

$$C_{14}H_7NO_4 + 4O + 8Cl = C_{12}Cl_4O_4 + 2CO_2 + NH_3 + 4HCl.$$

I obtained, by the direct action of the oxidizing mixture on indigo, only traces of chloranil.

In concluding, I wish to call the attention of chemists to the application of chlorate of potash as an oxidizing agent, for up to the present time it has been but seldom employed in organic chemistry, and yet the study of its action might in many cases lead to very remarkable results. I have treated *kinone*, which has lately become so interesting, in a similar manner to what has been stated, and found that it was transformed with the greatest facility into chloranil. In a future paper this subject will be examined more closely, and at the same time I shall throw out some hints concerning the relations of kinone to anilene, a base from which it can likewise be produced.

CXXII. *On the Decomposition of Oxides and Salts by Chlorine.* *By* Alexander W. Williamson, *Esq.*

THE compounds formed by the action of chlorine on the hydrates of the alkalies and earths have long since attracted the attention of chemists by their powerful bleaching properties. As they were produced by simply bringing together chlorine with the base in presence of water, they were at first considered as direct and simple combinations of chlorine with the oxide, and were therefore called oxychlorides.

Berzelius first showed this view to be untenable. He considered these compounds as containing a chloride and an oxygen salt of chlorine, the acid of which he assumed identical with that of Stadion, namely, 1 equivalent of chlorine to 3 of oxygen.

Serullas obtained by the evaporation of a solution of soda, which had been treated with chlorine, crystals of chloride of sodium, while the mother-liquid retained its bleaching properties unaltered. This experiment shows that a chloride and an oxygen salt of chlorine, which possesses the bleaching properties, are contained in these compounds.

By acting on the oxide of mercury with chlorine, Balard succeeded in obtaining a combination of oxygen with chlorine, which in its bleaching properties, as well as its salts, showed much resemblance to the oxygen acid supposed to be contained in the oxychlorides. He determined the composition of this acid at 1 equivalent chlorine to 1 of oxygen.

Millon has endeavoured to recall the ancient view with some

modification. He considers these compounds as analogous to peroxides, so that the atoms of oxygen which the peroxide of a metal contains beyond its oxide are here replaced by chlorine.

This view was but imperfectly refuted, and indeed the subject remained in considerable doubt until Gay-Lussac made known his interesting researches on the combinations of chlorine with bases.

I will here recall some of the principal facts, but must refer for further particulars to the original treatise of this great master.

If a mixture of a chloride with a corresponding salt of hypochlorous acid in their equivalent parts be treated with sulphuric acid in excess, chlorine is given off. If, on the contrary, the acid be added in a dilute state, and prevented by continual agitation from acting unduly on any particular part, and only so much acid be added as is sufficient to decompose the oxygen salt, then hypochlorous acid is alone set free, and can be distilled over unchanged. The so-called oxychlorides, when similarly treated, behave in the same manner.

The process in these instances is extremely simple, if we only recollect that hypochlorous acid with hydrochloric sets chlorine free by forming water; or, which is the same thing, the metal of the chloride deoxidates the hypochlorous acid in order to be able to combine as oxide with sulphuric acid, while from both the chlorine is set free.

In the second instance the salt of hypochlorous acid is alone decomposed, while no excess of sulphuric acid is present to cause a decomposition of the chloride.

Now if these oxychlorides were simple combinations of chlorine with oxide, the first drop of sulphuric acid would set free chlorine.

Founded on the correctness of this view, this great chemist has given us a method of preparing hypochlorous acid, far more practical than that formerly used. He distils the so-called chloride of lime with dilute nitric acid, which must be very carefully added in the manner above described, and distils off the hypochlorous acid. He confirms Balard's statement of its composition. Hypochlorous acid possesses, according to Gay-Lussac, the following properties:—It is a feeble acid, weaker perhaps than carbonic, although they mutually expel one another from their salts. Its salts have a great inclination to decompose into chlorides and chlorates. These salts, as such, possess no bleaching properties. In order to give a bleaching reaction, they must be decomposed by a stronger acid. They are partly decomposed by chlorine. Hypochlorous acid can be distilled over from any of these salts after treating it with chlorine.

I will now communicate some experiments which I have made on the action of chlorine on bases, and the products of this action. My principal object during these experiments was to become better acquainted with the manner of the formation, with the properties and decompositions of this most interesting compound, hypochlorous acid.

The experiments were performed in the laboratory at Giessen, and I had, during the course of them, the advantage of the presence and counsel of Professor Liebig.

The first point which I endeavoured to ascertain was the quantity of chlorine with which a base is capable of combining. Barytes was first subjected to this examination. A concentrated solution of this earth was saturated with chlorine by conducting a stream of the gas, which had been washed by water, slowly into it. This process was not considered complete until the liquid had assumed a strong colouring of chlorine. It was then agitated with a repeatedly renewed quantity of atmospheric air until no free chlorine could be perceived in it. This solution had the peculiar astringent taste of hypochlorous acid, and its powerful bleaching properties. It was oversaturated with ammonia and heated to the boiling-point, and having added an excess of nitric acid, it was precipitated by nitrate of silver. After separating it from this precipitate, the barytes was thrown down by sulphuric acid. Three determinations, conducted in this manner, gave the following results. For each determination a fresh liquid was prepared.

I. 0·550 chloride of silver = 0·136 chlorine.
0·243 sulphate of barytes = 0·159 barytes.
This gives 818 chlorine to 957 barytes.

II. 1·468 chloride of silver = 0·361 chlorine.
0·654 sulphate of barytes = 0·429 barytes.
This gives 805 chlorine to 957 barytes.

III. 1·836 chloride of silver = 0·453 chlorine.
0·781 sulphate of barytes = 0·513 barytes.
This gives 843 chlorine to 957 barytes.

The average of these three gives 822 chlorine to 957 barytes, or nearly 2 equivalents.

The question which now naturally presents itself is, in what manner can the chlorine be contained in this liquid, and in what combinations? The following experiments were instituted in order to ascertain this:—

To part of the original liquid a solution of nitrate of silver was added, by which a *pure white* precipitate of chloride of silver was formed, which increased by standing. Another portion was treated with barytes water until the smell and bleach-

ing reaction of hypochlorous acid had disappeared. Nitrate of silver now formed a black precipitate, which gradually decomposed, giving off oxygen.

The cause of this striking difference in the two reactions is evidently that in the first instance all the base was combined with chlorine in the form of chloride, while hypochlorous acid remaining free in the liquid, gradually increased the precipitate by its own decomposition. In the second case, the hypochlorous acid being combined with barytes gave the black precipitate, consisting of a mixture of chloride with peroxide of silver.

To test the correctness of this explanation the following experiments were made:—

Aqueous hypochlorous acid was neutralized with barytes. This salt possessed no bleaching properties. Carbonic acid precipitated carbonate of barytes. The liquid, after separation from the precipitate, was boiled until all free hypochlorous acid had disappeared. It now contained no traces of a hypochlorous acid salt, as proved by the fact that tincture of litmus was not bleached by it, though an excess of sulphuric acid was added, proving that the barytes salt was completely decomposed by carbonic acid.

A solution of barytes was saturated with chlorine in the manner above described, and being freed from superfluous chlorine, was now treated in a similar manner with carbonic acid. No precipitate whatever was formed, which must have been the case had any hypochlorous acid been combined with barytes. The hypochlorous acid salt, formed by the action of the first equivalent of chlorine with the base, had thus been entirely decomposed by the second equivalent.

When I further state, that on this liquid being subjected to distillation, hypochlorous acid passed over, while the residue consisted of chloride of barium with a small quantity of chlorate of barytes, then I think it will be beyond a doubt, that of the two equivalents of chlorine which the barytes took up, one combined with the barium, the other with its oxygen.

The following is the formula explaining the decomposition:

$$Aq + 2BaO + 2Cl = BaCl + BaOClO$$
$$Aq + 2BaO + 4Cl = 2BaCl + 2ClO$$

In endeavouring to purify this mixture, of chloride of barium and hypochlorous acid, from all free chlorine contained in it, I noticed a remarkable circumstance, which I will relate. By agitating the solution with repeatedly renewed portions of atmospheric air, I was able to obtain a colourless liquid, which possessed but a very slight smell of chlorine. But when this was allowed to stand for a few minutes, especially in a strong

light, the colour and smell of chlorine re-appeared. Now, as no chlorine had access to it from without, this must have been caused by a decomposition of the hypochlorous acid. This decomposition takes place in common daylight, more rapidly in direct sunshine, and most rapidly when the liquid is heated in a water-bath. The solution, after decomposition had ceased, and no more chlorine was given off, contained a considerable quantity of chlorate of barytes. The liquid now contained no hypochlorous acid, either free or combined. The following analysis was made in order to determine the proportion of chlorine remaining in it. The barytes was first precipitated by sulphate of soda. The chloric acid was then deoxidized by means of sulphurous acid, and after separation from the sulphate of barytes, the whole of the chlorine was determined by means of nitrate of silver, thus:—

Sulphate of barytes 1·597 = 0·940 barytes.
Chloride of silver 1·998 = 0·493 chlorine.

This is rather more than 1 eq. of chlorine.

I next endeavoured to ascertain the proportion of chloric acid in this amount. For this purpose a portion of the same liquid was precipitated by nitrate of silver, which gave the quantity of chlorine combined as chloride. After separating it from this precipitate the liquid was treated with phosphorous acid, which naturally precipitated metallic silver and a barytes salt, but also reduced the chloric acid. After heating for some time, the precipitates were dissolved in nitric acid, and the chloride of silver which formed, determined.

First precipitate of chloride of silver 4·992 = 1·182 chlorine.
Second precipitate ... ... 0·787 = 0·154 ...

This gives to 6 parts of chlorine as chloride, nearly 1 as chlorate. The theory requires to 5 of chloride 1 of chlorate; but part of the oxygen had probably escaped either free or as hypochlorous acid.

Having thus found that on treating barytes with chlorine the decomposition takes place in so simple a manner, I next endeavoured to find out whether the same laws would not hold good in the case of the alkalies. Of these I first chose potash, which was prepared by decomposing a solution of pure sulphate of potash by barytes water.

I. 4·051 of this solution gave 0·272 sulphate of potash = 0·107 potash, or 3·628 per cent. 18·819 were saturated with chlorine, in the same manner as the barytes had been, and gave, after reduction by ammonia and sulphurous acid, a precipitate of 3·314 chloride of silver = 0·818 chlorine.

Calculated to the amount of potash, this gives to 590 potash 706·5 chlorine, instead of 443, which is 1 equivalent.

II. 17·397 of the solution which was used for this determination gave 1·337 nitrate of potash = 0·6225 potash.

19·027 gave 3·031 chloride of silver = 0·748 chlorine, or in 590 potash 647 chlorine, instead of 443. The average of these two gives to 590 potash 677 chlorine, or to 2 eqs. of potash 3 of chlorine.

This liquid possessed the smell of hypochlorous acid as well as its bleaching properties. It contained no salt of hypochlorous acid, that is to say, that all this acid contained in it was in a free state, as was proved by the above-described reaction with silver.

A considerable quantity of chloric acid was contained in this liquid, but was not determined, as it depended only on the time allowed to elapse between the preparation of the liquid and its being made use of for analysis.

What now can be the cause of potash combining with a less quantity of chlorine than is the case with barytes? This arises probably from the stronger affinity of potash for chloric acid, which causes a decomposition of hypochlorous acid, by which chloric acid is formed and chlorine set free. Hence it is evident that by the formation of a small quantity of chloric acid the total quantity of chlorine in the liquid must be much diminished.

I now treated carbonate of potash in a similar manner with chlorine, and obtained the well-known liquid, possessing, from the first action of the chlorine, the smell and other properties of free hypochlorous acid, a considerable quantity of which was carried away by the escaping carbonic acid. Now, if this liquid be heated for some time in a water-bath, the hypochlorous acid is completely destroyed, chlorine is disengaged, and the liquid now contains a mixture of chloride of potassium with chlorate of potash. As the hypochlorous acid was from its first formation uncombined, the chloric acid must have, in all probability, been formed by a different process from that which took place in the preceding instance, where, by the action of chlorine on a hypochlorous acid salt, chloric acid formed, partly by taking the oxygen directly from the base, partly, perhaps, by a decomposition of hypochlorous acid. We here have a mixture of hypochlorous acid with chloride of potassium; after heating which we find part of the chloride of potassium is changed into chlorate of potash.

Now if this be the case, I must obtain the same result by treating a solution of chloride of potassium with hypochlorous acid. The experiment was made in the following manner:— In a concentrated aqueous solution of hypochlorous acid were dissolved crystals of chloride of potassium, and the mixture was

heated in a water-bath until chlorine ceased to be disengaged. This liquid deposited, on cooling, scales of chlorate of potash, which was also easily detected in the mother-liquid.

This process must not be considered as a direct oxidation of the chloride, for peroxide of hydrogen produces no such effect.

It is well known that aqueous hypochlorous acid has a great tendency, especially when heated, to form chloric acid, setting free chlorine. Now when chloride of potassium is present, this chloric acid, in the moment of its formation, decomposes the chloride, setting free its chlorine, the metal oxidating itself at the expense of hypochlorous acid.

On treating carbonate of soda with chlorine I obtained similar results, with the difference, that chloric acid formed even more easily than was the case with potash, and consequently the total content of chlorine in the liquid was less.

The following is an experiment showing the nature of this decomposition:—Treat a concentrated solution of simple carbonate of soda with chlorine until a considerable quantity of bicarbonate is precipitated, but not until this precipitate commences to be decomposed. The liquid on being now left to itself in the light continues for several hours to give off carbonic acid with slight effervescence. We here have carbonate of soda mixed with chloride of sodium and free hypochlorous acid. These two latter, by gradually acting on each other, in the manner above described, set chlorine free, which decomposes the carbonate.

Now, as by treating carbonates with chlorine hypochlorous acid is obtained free, and can be distilled over quickly, it appeared to me that this might be an easy method of obtaining this acid for use. It is desirable for this purpose to choose a base which has not too powerful an affinity for chloric acid, and consequently from the chloride of which, hypochlorous acid can be quickly distilled off without decomposition. I chose, with this view, carbonate of lime.

This salt, prepared for the purpose by precipitation, was mixed up with about 40 parts of water, and dissolved in chlorine. When quickly heated to the boiling-point, this liquid gave off its hypochlorous acid, while the residue in the retort consisted of a solution of chloride of calcium with a small quantity of chlorate of lime.

This is a cheap and easy method of preparing this most interesting compound. It is well if a slight excess of carbonate of lime be left in the liquid when subjected to distillation; it speedily dissolves as the liquid becomes hot, and the acid is thus obtained free from chlorine, which is not the case without this precaution.

I was induced from this to try the action of chlorine upon other salts with stronger acids, and discovered a series of interesting decompositions, of which I will here state the outline; and hope, after further investigation, to be soon able to communicate the details.

A solution of tribasic phosphate of soda was treated with chlorine, which it absorbed with great avidity. This solution, after saturation, possessed a strong smell of hypochlorous acid, which I distilled over from it. The residue gave a strongly acid reaction, proving that the chlorine had taken 2 atoms of soda from the phosphate, forming with the metal chloride of sodium, and with the oxygen hypochlorous acid.

Common phosphate of soda gave a similar result. The residue after distillation consisted of the same phosphate as the preceding, with 1 atom chloride of sodium.

Two basic pyrophosphates behaved in exactly the same manner.

The next salt I subjected to this treatment was sulphate of soda. A solution of this perfectly neutral salt was saturated at the common temperature with chlorine, which was freely absorbed by it. The liquid remained colourless, which shows that the chlorine absorbed was not contained, as such, in solution. This neutral sulphate of soda was indeed decomposed. The liquid, after saturation with chlorine, consisted of a mixture of bisulphate of soda with chloride of sodium and free hypochlorous acid. Whether any neutral sulphate remained undecomposed I have yet to ascertain. On being subjected to distillation, hypochlorous acid passed over at the beginning of the operation. The liquid which first distils contains most of the acid. Each successive portion contains less of it than the preceding. This compound possesses such powerful oxidating properties, far exceeding, at the common temperature, those of nitric acid, that it might doubtless become a valuable aid to the chemist in many of his operations. It might even be made advantageously on a large scale in the above-described manner; the same sulphate of soda would of course serve for many operations. It is only necessary to boil down the residue of distillation and heat it until all the chlorine is driven out as hydrochloric acid, which also need not be lost. It is now reconverted into neutral sulphate of soda, which can be redissolved and treated with chlorine as before.

The aqueous solution of hypochlorous acid may easily be prepared so as to contain in a given weight more bleaching power than the well-known lime compound. It will keep for a considerable time, even when concentrated, with but very little decomposition if protected from light, and, of course,

heat. I offer this as a hint for the consideration of manufacturers of bleaching powders. Should it prove a practical simplification of the method hitherto used for preparing the bleaching compounds, and thereby have any beneficial effect on the manufactures for which these are required, I shall feel myself amply rewarded.

The salts of sulphuric acid with the following bases are decomposed in like manner. Oxide of copper, peroxide of iron, oxide of zinc, protoxide of manganese, also the double salt of alumina and potash; even sulphate of lead, when suspended in water and treated in like manner, was slightly decomposed. Chromate of potash was also decomposed. Borax was entirely decomposed: the solution deposited after concentration crystals of boracic acid. Nitrate of potash slightly. Acetate of lead was decomposed, forming chloride and peroxide. These decompositions only take place in the presence of water. Crystallized sulphate of soda is not acted upon in its dry state by chlorine, though the crystals contain water.

Concluding from analogy that similar decompositions might be produced by cyanogen, I treated a solution of tribasic and common phosphate of soda with this gas: both were decomposed. The solution assumed a yellow colour, which by the further action of cyanogen became much darker. Upon distilling this liquid hydrocyanic acid passed over, and part of the above-mentioned yellow brown acid was precipitated in the residue in the form of a brownish substance, which probably contains the oxygen of the soda, for no cyanic acid was formed; but, as I have stated already, I hope to be soon able to communicate further particulars regarding these interesting decompositions.

CXXIII. *On some of the Substances which reduce Oxide of Silver and precipitate it on Glass in the form of a Metallic Mirror.* *By* JOHN STENHOUSE, *Ph.D.*

IT has long been known that aldehyde, when heated in a tube with ammonio-nitrate of silver, reduces the oxide to the metallic state, and forms a brilliant coating on the inner surface of the tube. Three other substances, saccharic acid, salicylic acid and pyromeconic acid, were also known to possess the same property, though the coatings which they yield are much darker, and therefore less beautiful than those formed by aldehyde. This was the state of our knowledge previous to the announcement, about six months ago, of Mr. Drayton's process for silvering mirrors in the cold, by means of ammo-

nio-nitrate of silver and an alcoholic solution of the oils of cloves and cassia.

I find that the number of substances which, especially when assisted by heat, give more or less brilliant coatings of reduced silver, is much greater than has hitherto been supposed. Thus grape-sugar forms a pretty brilliant mirror even in the cold. When unassisted by heat the mirror is rather slowly formed, requiring from six to twelve hours; but when a slight heat is applied it forms very readily in the course of a few minutes; the coating is much darker than that produced either by aldehyde or by Drayton's process. Cane-sugar also yields a mirror when assisted by heat, but none in the cold. Gum-arabic and starch also yield dark-coloured mirrors, but more slowly, and require considerable boiling: so do phloridzine and salicine. Oils of turpentine and laurel also give mirrors, but with still greater difficulty, the solutions requiring to be very concentrated. Resin of guaiacum acts in a similar manner.

Oil of pimento, as is well known, consists of two oils, one an acid oil, which is heavier than water, and forms crystalline compounds with the bases; this in the course of a few minutes, even in the cold, produces as brilliant a coating of silver as the mixture of the oils of cassia and cloves. The neutral portion of the pimento oil, which is lighter than water, does not reduce nitrate of silver even after long boiling. I could not succeed in forming metallic mirrors with cinnamic, benzoic, meconic, komenic, tannic or pyrogallic acids, with gum benzoin, elemi or olibanum, with oil of rhodium or with glycerine.

Ingenious as Mr. Drayton's patent process certainly is, it labours under a very serious inconvenience, which I greatly fear will not be easily remedied. In the course of a few weeks the surface of the mirrors formed by his process become dotted over with small brownish-red spots, which greatly injure their appearance. The cause of the spots seems to be this—that the metallic silver while being deposited on the surface of the glass carries down with it mechanically small quantities of a resinous matter, resulting, most probably, from the oxidation of the oil. This resinous matter, which is interposed between the glass and the silver, in the course of time begins to act on the metallic surface with which it is in contact, and to produce the small brown spots already mentioned. If an excess of the essential oils is employed to precipitate the silver, the metallic mirror is much darker, and gets sooner discoloured than usual. No doubt the alcohol present in the solution keeps up much of the resinous matter; still a little of it is almost always de-

posited on the silvered surface, and acts in the injurious way described.

CXXIV. *On the Decomposition of Salts of Ammonia at ordinary Temperatures.* *By* H. Bence Jones, M.D.

IT frequently happens that urine is met with which has become alkaline in consequence of the urea passing into carbonate of ammonia. Such urine, though at first showing an alkaline reaction on red or very slightly blue litmus paper, was observed, as it dried in the air, to have a well-marked acid reaction. By adding a slight excess of ammonia to healthy urine, or by leaving healthy urine to stand until it becomes alkaline, the above-mentioned reactions may always be observed. Slightly blue litmus paper is then at first made more strongly blue, and on drying in the air the paper becomes as red as if the urine were fresh, or no ammonia had been added.

This seemed to show that no free acid existed in the urine, but that the acid reaction was caused by some ammoniacal salt having this property of reddening litmus.

Pure urate of ammonia, when dissolved in water or with excess of ammonia, showed a similar reaction as the solution evaporated from the blue litmus paper, and hence it seemed probable that urate of ammonia was one cause of the acid reaction of the urine. Hippuric acid having been observed by Liebig to be present in healthy urine, I formed hippurate of ammonia with a slight excess of ammonia in the solution, and I found that when this dried on litmus paper it gave a strong acid reaction.

It occurred to me to make the same experiment with other salts of ammonia dissolved in cold water with an excess of ammonia, and I found in all a similar reaction. The salts used were the acetate, oxalate, nitrate, sulphate, hydrochlorate, hydrosulphate, benzoate, phosphate, and carbonate. The last produced much the feeblest acid reaction.

Some sulphate of ammonia was dissolved in water: at first it was neutral to test-paper; a drop of a solution of litmus was added to a small cupful of this solution; after standing some hours in the air the blue colour disappeared, and a pink solution was formed long before all the fluid had evaporated. The temperature was about 67° F.

The same experiment was repeated with urate of ammonia. A warm solution was made, and whilst warm it was poured into a basin with a drop of litmus solution; after standing eight hours a marked change of colour had taken place. A line of pink had formed where the fluid had evaporated, and

there was a decided pink tint in the violet-coloured solution. After twelve hours no violet colour was seen, but a well-marked pink tint. The temperature was rather lower than in the previous experiment.

A solution of urate of ammonia when cold was filtered into a watch-glass: on examining the edge of the fluid as it evaporated a granular deposit mixed with very small needles was seen with the microscope, and single crystals and tufts of crystals of uric acid were present in considerable numbers.

Another solution was made with a marked excess of ammonia: on evaporation in a watch-glass, uric acid crystals, as before, were found at the edge.

To avoid the interference of the atmosphere, solutions of urate of ammonia and chloride of ammonium, coloured blue with litmus, were evaporated in a very perfect vacuum over chloride of calcium. The solution of chloride of ammonium became red in less than five hours. The solution of urate of ammonia formed a red edge, where the fluid evaporated, in half an hour; this continued to grow broader, and after fourteen hours the basin was dry, leaving a broad red deposit on the side.

Two solutions of equal quantities of chloride of ammonium were made, the one in alcohol, the other in water. They were both coloured with blue litmus and left to evaporate in the air. The alcoholic solution became red the soonest.

These experiments show that salts of ammonia are decomposed by evaporation at ordinary temperatures. It was long since observed by Sir H. Davy, that if the same quantity of nitrate of ammonia was dissolved in much and little water, the loss on evaporation by boiling was directly in proportion to the quantity of water used. Part was probably carried off by the steam, but the above experiments show that it was partly decomposed, the ammonia being separated from its combination with nitric acid.

H. Rose also observed the decomposition of the sulphate of ammonia when evaporated at a boiling temperature. He says, "If the boiling is effected in a retort a liquid passes over into the receiver, which contains free ammonia. This result evidently arises from the water as base eliminating the oxide of ammonium from its combination with sulphuric acid and combining with the same. The quantity of the sulphate of the oxide of ammonium decomposed in this way is indeed small, but it must also be remembered that the oxide of ammonium is one of the most powerful bases, and this result is chiefly to be ascribed to its greater volatility *."

* Taylor's Scientific Memoirs, vol. ii. p. 371.

It seems probable that the act of evaporation of the fluid, in which the salt is dissolved, assists the escape of the oxide of ammonium from its combinations, the alcoholic solution of chloride of ammonium becoming more quickly acid than the watery solution.

The decomposition of ammoniacal salts, although so very perceptible to test-paper (as may be best seen by dipping blue litmus paper into an ammoniacal solution of chloride of ammonium and drying in the air), is scarcely perceptible to balance.

Nitrate of ammonia loses, according to Sir H. Davy, from 3 to 6 grs. per cent. when the temperature of evaporation is 212° F. During the evaporation of a solution of spec. grav. 1·146 and 1·15, at a temperature below 120°, he never detected any loss *.

Chloride of ammonium may be evaporated in a water-bath without perceptible loss.

* On Nitrous Oxide, p. 51. ed. 1839.

December 16, 1844.—The President in the Chair.

Dr. Augustus W. Hofmann presented a specimen of Chloranil prepared from Salicine; and John Turner, Esq., a specimen of Rangoon Petroleum to the Society's Museum.

The Rev. Vernon Harcourt, M.A., F.R S., J. Pereira, M.D., F.R.S., William Sands Coxe, Esq., F.R.S., John Birt Davis, M.D., John Woolrich, Esq., and T. H. Barker, Esq., were duly elected Members.

The following communications were then read:—

CXXV. *On some commercial Specimens of Green Glass.* By Robert Warington, *Esq.*

SOME short time since some green glass wine bottles were put into my hands for examination, the inner surface of which was covered with a thin film, having a dull and slightly opake appearance. The question to be solved was, the possibility of removing this so as to restore the glass to its original transparency. My first impression, from the general appearance of the bottles, was that this dullness was to be attributed to some matter mechanically adherent to the surface, and that it probably arose from their having been washed with foul, greasy, or soapy water; but on examination this was found not to be the case, the surface of the glass having been evidently affected by the action of some corroding agent. Portions of the glass were therefore submitted to the action of a weak solution of tartaric acid, as the acid most likely to be present in wines; and in the course of twenty-four hours, the vessel, in which the digestion was conducted, was one-fourth part full of beautiful crystals of bitartrate of lime. It was also strongly acted upon by diluted hydrochloric acid, forming a solution of chloride of calcium, and a gelatinous mass from the hydration of the silicic acid. From these preliminary experiments it was evident that a great excess of lime had been employed in the manufacture of the glass, and this had rendered it totally unfit for any of the ordinary purposes to which such bottles are applied. The glass was then submitted to analysis, and as the routine followed, in this and the subsequent case, was similar to that adopted in the examination of all such compounds, I shall not detain the Society by going through the detail; suffice it to say, that the alkalies, soda and potash were separated by the fluoric acid process, and the potash estimated from the weighed quantity of the mixed sulphates thus obtained, by means of the double chloride of platinum and potassium.

The results, calculated to the 100 parts, are as follows:—

Silica	49·00
Lime	24·75
Soda	7·25
Potash	2·00
Oxide of iron	10·10
Alumina	4·10
Magnesia	2·00
Oxides of copper and manganese	a trace
	99·20

On making additional inquiries concerning these bottles, I found that they were offered to the consumer, the wine merchant, at a lower price than the ordinary wine bottles, and that the vendors urged strongly the superiority of their goods under the recommendation that they caused port wine to deposit its crust much sooner and firmer, that is, adhering more tightly to the bottle, than would be the case where the common glass was employed. One gentleman had been a loser to a considerable amount from bottling a large quantity of white wine in these vessels, the bottles having become clouded, and the flavour of the wine, as a matter of consequence, being materially affected. As it was a question of scientific interest to ascertain to what extent the foregoing glass differed from our ordinary green glass of commerce, as occurring in the form of wine bottles, an analysis of this was undertaken, and the following are the results, calculated as before to the 100 parts:—

Silica	59·00
Lime	19·90
Soda	10·00
Potash	1·70
Oxide of iron	7·00
Alumina	1·20
Magnesia	0·50
Oxide of manganese	a trace
	99·30

On comparing these results with the former, it will be seen that the total amount of bases present is far less, and calculating them out as silicates, the first analysis will show a deficiency of silicic acid amounting to about 20 parts on the 100.

It was about the period of this examination being terminated, that Professor Faraday, in a lecture at the Royal Institution on the manufacture of glass mirrors, exhibited a French glass bottle which had been subjected accidentally by Mr. Pepys, jun. to the action of diluted sulphuric acid, in the pro-

portions of 1 of acid to 10 of water; in a short time this had, by its action on the glass, produced a most extraordinary and beautiful crystallization of sulphate of lime in small, detached, and rounded pyramidal masses, tightly adherent to the surface of the bottle. In consequence of this curious action, I was induced to submit the bottles under notice to a similar mixture, and after having been filled and loosely corked they were put aside in a place of safety. In the course of two or three weeks I was surprised one morning to find the floor of the laboratory covered with wet, which had apparently run from the direction where these bottles had been deposited, and on examination they were found to be cracked in all directions, the fissures being covered with a deposit of gelatinous silica: on breaking one of these, the whole internal surface was found lined, for the thickness of about one-fourth of an inch, with a mixture of sulphate of lime and silica, the crystallization of which had evidently caused the fracture of the bottles; in some places the glass was corroded completely through its substance.

CXXVI. *On certain Processes in which Anilene is formed.* *By* Drs. J. S. Muspratt and A. W. Hofmann.

NOTWITHSTANDING the laborious endeavours that have been made of late years to enable us to foretell the metamorphoses which a given organic compound should sustain under the influence of different chemical agents, still it must be admitted that we have by no means succeeded in establishing antecedently, with absolute certainty, the *modus operandi* of a decomposition; we have only arrived at some main features, giving us an insight as to the probable result of an experiment we are about to perform.

It is known, for example, that by the action of chlorine or bromine a number of equivalents of hydrogen is replaced; that phosphoric acid eliminates the elements of water; and that by treating a compound with caustic barytes, carbon and oxygen are abstracted in the form of carbonic acid. There are many instances, however, where no change occurs, or if so, it is at least quite dissimilar.

The fundamental cause of this uncertainty lies in the deficiency of our present knowledge respecting the true constitution of organic bodies.

Hitherto the simplest decompositions known are those effected by powerful agents and with the cooperation of very high temperatures. In such cases the chemical constitution

of the substance decomposed influences the nature of the products far less than the composition and affinities of the elements of the decomposing body.

In regard to this some observations deserving of attention have been recently made which particularly gave origin to the researches described in the present treatise.

It has been ascertained, namely, that bodies possessing *the same composition but very different constitutions*, when submitted to the influence of strong agents, suffer frequently *the same decomposition*.

One of the most remarkable examples of this kind was lately remarked by Cahours.

Some years since Laurent * obtained by the action of ordinary nitric acid upon the oil of *Artemisia dracunculus*, a body containing no nitrogen, the *draconic acid*, which is expressed by the annexed formula:

$$C_{16}\,H_8\,O_6.$$

Previous to this Cahours † had converted in a similar manner, oil of anise (from *Pimpinella anisum*) into *anisic acid*, for the composition of which he gave the formula $C_{16}\,H_7\,O_6$.

In consequence of a discussion between Gerhardt ‡ and Laurent §, this acid was afterwards recognised as identical with the draconic.

When distilled with an excess of barytes, the draconic or anisic acid yields a colourless liquid, named *dracole* by Laurent and *anisole* by Cahours. The transformation is very simple, two atoms of carbonic acid being removed by the oxide of barium.

$$\underbrace{C_{16}\,H_8\,O_6}_{\text{Draconic acid. Anisic acid.}} + 2\,BaO, \text{ giving } \underbrace{C_{14}\,H_8\,O_2}_{\text{Dracole. Anisole.}} \text{ and } 2\,BaO + 2CO_2.$$

Through the beautiful investigation which Cahours ‖ has lately published on the oil of *Gaultheria procumbens*, we have become acquainted with the methyle compound of salicylic acid, which is remarkable for possessing the same composition as draconic acid.

$$\underbrace{C_{14}\,H_5\,O_5\,,\,C_2\,H_3\,O}_{\text{Salicylate of oxide of methyle.}} = \underbrace{C_{16}\,H_8\,O_6}_{\text{Draconic acid.}}.$$

It was worth while to investigate in a comparative manner

* *Revue Scient.*, t. x. p. 6.

† *Ann. de Chim. et de Phys.*, 3 ser. t. ii. p. 274, and *Annal. der Chem. und Pharm*, bd. xli. s. 66.

‡ *Revue Scient.*, t. x. p. 184. § Ibid. p. 362.

‖ *Ann. de Chim. et de Phys.*, 3 ser. t. x. p. 327, and *Annal. der Chem. und Pharm.*, bd. xlviii. s. 6

the action of barytes upon this body. The experiment was performed by Cahours, who ascertained that the oil of *Gaultheria procumbens* undergoes exactly the same metamorphosis as draconic acid.

The draconic acid and the salicylate of oxide of methyle are two compounds whose constitutions could not be imagined more at variance with each other; nevertheless we see that under the influence of a high temperature and the powerful cooperation of barytes, they yield exactly the same product.

After the foregoing, it appeared to us to involve sufficient interest to compare the products of decomposition which other *isomeric bodies* furnish under the same circumstances; and, indeed, some experiments made in the laboratory of Giessen have led to results which perhaps are not unworthy of communication.

Fritzsche*, in his investigation upon the action of potash on indigo, discovered, as is well known, the anthranilic acid, having the formula $C_{14}\,H_7\,NO_4$, which when distilled rapidly *per se*, or with lime, furnishes anilene and carbonic acid.

$$\underbrace{C_{14}\,H_7\,NO_4}_{\text{Anthranilic acid.}} + 2\,CaO, \text{ yielding } \underbrace{C_{12}\,H_7\,N}_{\text{Anilene.}} + 2\,CaO + 2\,CO_2.$$

Investigations recently made, in quite another department of organic chemistry, have presented us with two other bodies whose composition agrees also with the formula of anthranilic acid.

Cahours once observed, during his researches upon the oil of gaultheria, that the salicylate of oxide of methyle by the action of ammonia is converted into salicylanide, a compound *isomeric* with anthranilic acid.

$$\underbrace{C_{14}\,H_5\,O_4 + NH^2}_{\text{Salicylanide.}} = \underbrace{C_{14}\,H_7\,NO_4}_{\text{Anthranilic acid.}}.$$

Deville† had beforehand discovered, as one of the products of the distillation of tolu balsam, a carbo-hydrogen possessing the greatest similarity with Faraday's tri-carburet of hydrogen (benzin-benzole), which he called *benzoene*; and for which Berzelius‡ afterwards proposed the name *toluine*. This body, which according to Deville's analysis is represented by the formula $C_{14}\,H_8$, when heated with fuming nitric acid, loses, similarly to benzin, one equivalent of hydrogen, which is re-

* *Bullet. Scient. de St. Pétersb.*, t. viii., and *Ann. der Chem. und Pharm.*, bd. xxxix. s. 96.

† *Annal. de Chim. et de Phys.*, 3 ser. t. iii. p. 151, and *Annal. der Chem. und Pharm.*, bd. xliv. s. 304.

‡ *Jahresbericht*, xxii. s. 254.

placed by the elements of peroxide of nitrogen; the resulting compound is *protonitrobenzoene*,—Laurent's nitrobenzoenase and Berzelius's nitrotoluid,—and possesses likewise the same composition as anthranilic acid.

$$\underbrace{C_{14}H_8}_{\text{Benzoene.}} + NO_5 \text{ giving } \underbrace{C_{14}H_7NO_4}_{\text{Protonitrobenzoene.}} + HO.$$

In relation to salicylamide, it is requisite to mention here some researches antecedently performed by Gerhardt*. Before this substance was discovered, the products of the distillation of salicylate of oxide of ammonium were investigated by that chemist, with the view to obtain anthranilic acid, or at least anilene.

$$\underbrace{C_{14}H_5O_5 + NH_4O}_{\text{Salicylate of oxide of ammonium.}} = \underbrace{C_{14}H_7NO_4}_{\text{Anthranilic acid.}} + 2HO.$$

A transformation of the above kind would have possessed some similarity with the conversion of oxalate of ammonia into oxamic acid; the decomposition, however, takes place in quite another way; the salt evolves first all its ammonia, then the acid undergoes a metamorphosis, which Cahours previously foretold when working upon oil of anise, namely, that the salicylic acid separates into carbonic acid and hydrate of phenyle (phenol).

$$\underbrace{C_{14}H_5O_5, NH_4O}_{\text{Salicylate of oxide of ammonium.}} = NH_3 + 2CO_2 + \underbrace{C_{12}H_5O + HO.}_{\text{Hydrate of phenyle.}}$$

The possibility of salicylamide yielding anilene was much more likely; for if we regard the latter as the amide of phenyle, it was to be expected that, by decomposition, it would afford the amide compound of the same radical as we get by the distillation of the acid, the oxygen compound of phenyle.

$$\underbrace{C_{14}H_5O_5, HO}_{\text{Hydrated salicylic acid.}} = \underbrace{C_{12}H_5O, HO}_{\text{Hydrated oxide of phenyle.}} + 2CO_2.$$

$$\underbrace{C_{14}H_5O_4, Ad}_{\text{Salicylamide.}} = \underbrace{C_{12}H_5Ad}_{\text{Phenamide.}} + 2CO_2.$$

We prepared, therefore, a large quantity of salicylamide, according to the method prescribed by Cahours. The crystalline substance, fused at a low heat to expel any adhering water, was introduced into the closed end of a combustion tube, the fore part of which we filled with caustic lime. After heating the lime to incipient redness, the vapour of the salicylamide was allowed to permeate it. Some moisture from

* *Annal. der Chem. und Pharm.*, bd. xlv. s. 24.

the lime condensed in the recipient, upon which floated brownish drops of oil; there was besides given off a large quantity of ammonia at the same time that a considerable portion of carbon deposited in the tube.

The distillate, when mixed with an excess of hypochlorite of lime, afforded immediately the blue colour so characteristic of anilene, while a chip of fir-wood moistened with an acid and then immersed in the oil partook of a deep orange-yellow tinge.

When a portion of the distillate, however, was supersaturated with hydrochloric acid, only a minute quantity of the oil dissolved; what remained intact, from its smell and its solubility in potash, &c., manifested itself to be hydrate of phenyle. The mixture was allowed to percolate a moist filter and the filtrate distilled with hydrate of potash. During this process a fluid trickled from the retort, which gave with hypochlorate of lime the *evident* reaction of anilene. The quantity of the base obtained from this source is, however, extremely small. We have repeated the experiment in many ways, *e. g.* instead of lime caustic barytes was taken, or the vapour of the salicylamide was conducted through a heated tube filled with pounded glass only. In nearly all these cases nothing but hydrate of phenyle was obtained; ammonia being formed at the expense of a portion of the decomposed substance, whilst the superfluous hydrogen passed off, most likely, in the state of a hydrocarburet.

Had it not been for the extreme delicacy of the hypochlorite of lime test, it would have been utterly impossible to detect anilene among the products of the distillation of salicylamide. Quite another result took place when we submitted protonitrobenzoene to the same treatment. This substance, which we had prepared in large quantities for the purpose of another investigation, soon to be communicated to your Society, was conducted over glowing lime. A dark yellow oil distilled over, which was almost completely soluble in hydrochloric acid. The undissolved portion was some protonitrobenzoene which had escaped decomposition. In order to remove it we agitated the acid solution with æther, in which medium the uncombined oil dissolved, and after taking off the æthereal solution with a pipette, we boiled the remainder to expel the last traces of nitrobenzoene.

We next distilled the purified liquid with hydrate of potash, and obtained a colourless mobile oil which collected in a homogeneous layer upon the surface of the water. This fluid was soon recognised as *pure anilene.* It would have been very easy for us to have produced a sufficient quantity of the

base for a combustion, but we concluded that an analysis would be quite superfluous, as the properties of this body are so characteristically marked.

The oil obtained in the above manner was readily soluble in mineral and organic acids, and on the addition of an alkali reappeared; perchloride of platinum produced, in the hydrochloric acid solution of the base, a beautiful yellow crystalline deposit; the oil, when brought in contact with concentrated hydrochloric, sulphuric, or nitric acids, inspissated, forming a dense crystalline mass, which, when redissolved, coloured fir-wood and elder-pith intensely yellow; with hypochlorite of lime the characteristic violet colouring appeared, which was also the case with fuming nitric acid; and lastly, with a solution of chromic acid it afforded the bluish-green deposit, which Fritzsche gives as a sure indication of anilene.

All these reactions showed infallibly that the nitrobenzoene, when subjected to the united influence of lime and a high temperature, affords the same decomposition as anthranilic acid under the same circumstances.

We could not succeed in obtaining anilene by passing the vapour of nitrobenzoene through a heated tube, finding that when the temperature is not very high, the oil distils over unchanged, while, if the heat is great, the whole is consumed, forming a dense brownish-black cloud. We recognised, nevertheless, the formation of anilene in an unquestionable manner, by distilling nitrobenzoene with an alcoholic solution of potash, in order to procure the substance corresponding to Mitscherlich's azobenzide, for on adding hypochlorite of lime to the distillate which contained the red crystals of azobenzoéne (?), a beautiful purple reaction ensued.

The formation of anilene in this manner affords, perhaps, a new mode for obtaining bodies possessing basic properties, which we intend studying in conjunction with the products of decomposition of *nitrobenzide* and a few other analogous compounds.

January 6, 1845.—Thomas Graham, Esq., Vice-President, in the Chair.

Dr. Muspratt presented his translation of Plattner's work on the Blowpipe.

Thomas Ransom, Esq., John Eddowes Bowman, Esq., G. W. Mowbray, Esq., Charles Askin, Esq., William Sykes Ward, Esq., Stan. Desussex, Esq., J. Cooper, Esq., and John Graham, Esq., were duly elected Members.

The following paper was then read:—

CXXVII. *Observations on the Decomposition of Metallic Salts by an Electric Current.* By Mr. James Napier.

IN the paper I had the honour of reading before the Chemical Society at the close of the last session upon this subject, I stated my intention of bringing under their notice, in a series of short papers, such phænomena as seemed interesting which might present themselves in my daily avocations. In fulfilling this promise, I must beg leave to remind the Society that they are phænomena observed during the practical application of electro-metallurgy on the large scale, most of which are apparently at variance with many of the prescribed fundamental laws of electro-chemical decomposition, such as that referred to in my last communication, the non-transference of the base of an electrolyte, a subject I intend to discuss in a separate paper at an early opportunity. Some of the experiments were made on a small scale with different electrolytes from those used on the large scale, in order both to verify the results of practice and to ascertain if they were confined to the electrolytes there employed, which are the double cyanides of gold, silver and copper, with potassium. Some of these experiments will be given in detail.

It is laid down as a fundamental law in electro-decomposition, that there can be no inequality of force in any part of a voltaic current, and that the decompositions dependent upon the current are always in definite proportions, so that the amount of any element or salt radical liberated at one electrode is an exact equivalent of another element or salt radical liberated at the opposite electrode. But the results of experience in the deposition of metals from the above-named salts have induced the electro-metallurgist to follow another law somewhat at variance with that laid down by electro-chemists, and which enables him to strengthen or weaken his solution of metal at pleasure. Indeed there is no law which appears to him more definite than that, if a large positive and small negative electrode be used, there will be more dissolved from the former than is deposited upon the latter; and on the contrary, if a large negative and small positive electrode be used, more will be deposited upon the negative than is dissolved from the positive.

Being aware of the decided manner in which electro-chemists have laid down the law of the decomposition of electrolytes in definite proportions, I at first looked upon the results of practical experience with doubt, and in order to put it to the test, and to ascertain whether the discrepancy was accidental or not, I adopted the following practice:—the positive

electrode was carefully weighed every morning, previous to immersing it in the gilding or plating solution, and again when taken out in the evening, and the loss compared with the amount deposited, an account of which was accurately taken. This practice was continued for upwards of nine months, varying at times, as far as practicable, the relative sizes of the two electrodes and the condition of the solutions, and during this period there were only five trials where the loss from the positive was exactly the amount of the gain on the negative. In many cases the difference did not exceed 3 per cent., but the average difference was 25 per cent., and occasionally as high as 50 per cent., varying in a great measure with the condition of the solution and the relative sizes of the electrodes.

During these operations two questions suggested themselves as of importance; namely, Is this discrepancy of equivalent electrolyzation confined to the double cyanides of the metals? and second, Does the amount of electricity, as indicated by the oxidation of the zinc in the battery, correspond with the amount of metal deposited upon the negative electrode, or the quantity dissolved from the positive?

I had observed, while making some experiments upon the relative endosmose of different substances, that if sulphate of copper be used in one division of a decomposition cell in which the negative electrode is placed, the other division being charged with water acidulated with hydrochloric acid, and a copper positive electrode immersed, there is dissolved in the positive cell an equivalent of copper for that deposited upon the negative pole, but there is formed besides a great quantity of white powder resembling a subchloride of copper, slightly soluble in water, which adheres to the pole with great tenacity, sometimes, if the current be continued several hours, to the depth of $\frac{1}{16}$th of an inch, by which means the positive pole will lose, according to the strength of acid and the power of battery, from $1\frac{1}{2}$ to 3 times the quantity of that deposited upon the negative electrode.

The substance formed and collected upon the pole I have not yet had an opportunity of analysing, but its general properties differ from those of the chloride or subchloride of copper; it is white when newly formed, but becomes green by washing and exposure to the air, and then slightly deliquescent. It gives an immediate deep blue colour with ammonia, dissolves in nitric acid with effervescence, also in hydrochloric acid, and is not precipitated by dilution, but is converted into the chloride: 25 grains gave 6·3 grs. of chlorine and 11·8 grs. of copper; it is probably an oxychloride.

By way of comparing these results with the practical ex-

perience alluded to, I instituted a series of small experiments, in which the second question referred to was particularly noticed; a few of these I will state in detail.

400 grains of cyanide of potassium were dissolved in 12 ounces of distilled water, divided into equal parts and placed in the two divisions of a decomposing apparatus, being separated by a porous diaphragm; silver electrodes of equal size were put into each and connected with a battery of 9 pairs of zinc and copper plates; the negative division was so constructed that the gas evolved from the electrode was received into a graduated jar; the current was continued until 25 cubic inches of gas were obtained; the two electrodes were then weighed; the negative was found unchanged, the positive had lost 62 grains, which is 8 grains more than the equivalent of hydrogen evolved.

The same experiment was repeated with 600 grains of cyanide of potassium to the 12 ounces of water; the positive electrode in this instance had lost 70·5 grs., being 16·5 grs. more than the equivalent of gas evolved.

Again repeated, having 800 grs. of cyanide of potassium, when the positive electrode had lost 85 grs., or 31 grs. more than the equivalent of gas evolved. The waste or destruction of zinc in the battery for these three experiments, amounted to 506 grs., which is more than an equivalent of zinc for the gas evolved at the negative pole, but is not an equivalent for the silver dissolved from the positive.

In case of any absorption of gas in the negative cell producing an erroneous result, I charged the negative division with a solution of sulphate of copper, in which was immersed a copper electrode, the amount of metal deposited being taken as the measure of electrolyzation in this cell; the positive division was charged with a solution of cyanide of potassium, in which was placed a silver electrode, the whole being attached to a single pair of zinc and copper elements excited by a solution of sal-ammoniac. In the three following experiments the current was only continued one hour for each:—

	I.	II.	III.
Copper deposited on the negative electrode	5·0 grs.	6·2 grs.	5·5 grs.
Silver dissolved from the positive electrode	37·0 ...	39·3 ...	40·7 ...
Zinc dissolved in the battery	5·8 ...	6·5 ...	6·3 ...

In these experiments we have nearly two equivalents more dissolved from the positive pole than is deposited upon the negative.

Another experiment with the same electrolytes, but both positive and negative electrodes being pure copper, the current was continued for sixteen hours,—

The negative electrode had gained . 22 grs.
The positive electrode had lost . . 75 ...
The zinc dissolved in the battery was 25 ...

Here we have upwards of three equivalents dissolved from the positive pole to one deposited upon the negative; in all these experiments the cyanide of potassium was in the proportion of 40 grs. to the ounce of water.

In the three following experiments hydrochloric acid was used in the positive division instead of cyanide of potassium, the negative containing a solution of sulphate of copper; the battery consisted of a single pair excited with a solution of common salt:—

I. Hydrochloric acid in the proportion of 1 ounce to 12 of water, the current kept up for eighteen hours,—

Deposited upon the negative electrode 15 grs.
Dissolved from the positive electrode . 22 ...
Zinc dissolved in the battery . . . 18 ...

II. Hydrochloric acid, 2 to 12 of water, current passing for twenty-four hours, —

Deposited upon the negative electrode 40 grs.
Dissolved from the positive electrode . 62 ...
Zinc dissolved in the battery . . . 48 ...

III. Hydrochloric acid, 3 to 12 of water, current passing for twenty-four hours,—

Deposited upon the negative electrode 47 grs.
Dissolved from the positive electrode . 87 ...
Zinc dissolved in the battery . . . 50 ...

Similar experiments were made with the positive division charged with a solution of chloride of sodium, chloride of potassium, chloride of ammonium and several other chlorides, in the whole of which there was more dissolved from the positive electrode than was deposited on the negative. With dilute sulphuric acid, sulphate of copper, or any of the soluble sulphates, in the positive division, the quantity deposited was exactly equivalent to that dissolved from the positive, except where the current was continued for several days, when the positive electrode was slightly covered with a black gelatinous substance, supposed by some to be oxide of copper, formed from an imperfect transfer of the sulphuric acid, which leaves it undissolved; but in such cases I have always found an equivalent of copper held in solution to that deposited, this black matter being also formed. I do not refer here to the black matter which is a constant attendant when impure copper or salts of copper are used, and which is in a great measure caused by the iron in the salt or in the metal forming the

electrode. When the nitrates were used in the positive division, the results were the same as with the sulphates, and when long continued, a little brownish matter was formed on the positive electrode, and there was consequently more dissolved from the positive than was deposited on the negative.

When 1 part of nitric acid was used to 12 of water, there was nearly one-fourth more dissolved from the positive than was deposited upon the negative, although a piece of copper put into acid of the same strength and for the same length of time as the battery was in action, was not perceptibly acted upon. Other phænomena were observed during these experiments, which I shall take occasion to notice on a future opportunity, but will now offer a few general remarks upon the results detailed. In the first place it may be stated generally, that when the double cyanides are the electrolytes, the amount of metal liberated at the cathode and dissolved from the anode is not in equivalent proportions, but varies according to their relative size and the condition of the solution; when the solutions are neutral, there is a tendency in favour of more being deposited upon the cathode than is dissolved from the anode, even when they are equal in size; and when there is an excess of cyanide of potassium, the tendency is great for the solution of more from the positive than what is deposited on the negative electrode. If, for example, the positive is made to surround the negative, exposing about three times more surface, there will be an average of one-third more dissolved than is deposited; and if, on the contrary, we deposit on the inside of the vessel, the positive pole being suspended within, there will be about one-fourth more deposited upon the article than what is dissolved from the pole; but of course this always varies with the condition of the solution.

From these, and some of the experiments with cyanide of potassium, hydrochloric acid and the chlorides, it is evident with such electrolytes, that when electrodes are used which combine with the elements set free, the amount liberated or combined with one electrode is not a measure of that liberated at or combined with the opposite electrode; but we must observe, as the result of experience, that the element liberated at the negative electrode is a proper measure of the amount of electricity passing through the electrolyte, if that electrolyte be composed of 1 equivalent of base and 1 of acid, or of single equivalents of elements; but if a subsalt be the electrolyte, there will be two proportions liberated at the negative for one proportion of zinc destroyed in the battery; and if a trisubsalt be used, 3 equivalents will be deposited, &c.; all electrolytes being decomposed as if they were constituted of two elements.

It may be remarked in the second place, from these results, that the stronger the solution of cyanide of potassium is, there is comparatively more dissolved from the positive electrode; that this may arise from the metals used as electrodes being very soluble in that menstruum, and that the difference between the electrodes is simply the result of this solubility; that it is the result of solubility rather than direct electrolysis, the experiments detailed fully show; but that the electricity influences this solubility I think evident. Pieces of gold, silver and copper, of the same dimensions with the positive electrode, were immersed in solutions of cyanide of potassium, of the same strength with that used in the experimental cell, and kept in the same length of time. When the gold positive electrode had lost 59 grs. above the equivalent of what was deposited upon the negative, the gold plate in solution of cyanide of potassium had only lost one half-grain, and required eight weeks to lose 59 grs.

When the silver positive electrode had lost 96 grs. over an equivalent of that deposited on the negative, the plate immersed in solution of cyanide of potassium had lost 3 grs., and required twenty-nine days to lose 96 grs.

When the copper positive electrode had lost 32 grs. more than the amount deposited upon the negative, the copper plate in solution of cyanide of potassium had lost 2 grs., and required twelve days to lose 32 grs.; the copper was comparatively quicker in being dissolved.

The same tendency in the positive electrode to dissolve was exhibited with the hydrochloric acid, increasing according to the strength of the acid. It was also manifest in all the chlorides; indeed every electrolyte tried indicated this tendency to a certain extent; the metals used as electrolytes were pure. Whether this increased tendency in the metals to dissolve, when made the positive electrode, be an exalted affinity excited between the metal and the negative element of the electrolyte, we will not as yet venture to assert, although the facts bear evidence to this; and if so, we think it favours the argument, that chemical action is the result of electricity, rather than electricity being the result of chemical action. But there being many phænomena in the practice of electro-metallurgy favourable to this view, I will leave the further notice of this subject till opportunity enables me to bring these facts under your notice.

January 20, 1845.—The President in the Chair.

M. Claudet exhibited numerous specimens illustrative of the late improvements in printing from a Daguerreotyped picture, and in Photography generally.

William Richardson, Esq. was elected a Member of the Society.

The following communication was then read:—

CXXVIII. *On the Distilled Waters of our Pharmacopœias.* *By* Robert Warington, *Esq.*

THE subject of flavoured waters, prepared by distillation or extemporaneously, through the medium of carbonate of magnesia, has for some time past engaged my attention; and as it is a question of considerable importance to the pharmaceutical chemist, I am induced to lay the detailed investigation before the Society.

The formulæ given for the preparation of distilled waters in the London Pharmacopœia of 1836 is as follows:—To a specified quantity of material, whether it be essential oil, flowers, herbs, bark or berries, let 2 gallons of water and 7 oz. of proof spirit, having a specific gravity 0·920, be added, and submit the mixture to the process of distillation until one gallon shall have passed over. Presuming that the entire amount of spirit employed passes over in this operation, the resulting product will contain a quantity that will be equivalent to about $4\frac{1}{2}$ oz. of rectified spirit of spec. grav. 0·838.

The Edinburgh form has rather less spirit to the proportion of materials, 2 gallons of water and 3 oz. of rectified spirit are so employed, and a gallon distilled.

The Dublin formula differs from the foregoing, in ordering half an ounce of rectified spirit to be added to each pound of the water after distillation, or in the ratio of 5 oz. to the gallon.

In the course of other investigations, some years since, I found that when a very small quantity of alcohol was added to distilled water, and the mixture kept exposed to the air for a length of time, the containing vessel being carefully covered with paper to exclude the dust, it became gradually converted into acetic acid, and, by analogy, I was led to believe that the same effect would take place in these distilled waters; the following experiments were therefore put in operation to test the accuracy of these ideas.

In the distillation of essential oils, it is well known that the water which passes over is opalescent from its being highly charged with the oil, and that when thus impregnated, it will keep perfectly sound for a great length of time. Distilled waters were prepared from various of the essential oils without

the addition of any spirit, and these were taken as the basis of the following experiments.

Equal portions of the waters obtained from the oils of dill, carraway, pimento, spearmint and cinnamon were taken, and to one-half the proportion of spirit ordered by the London College was added, the other half remaining in its original state; these were all loosely corked, marked, and placed aside. After remaining six months they were examined, when the spearmint and carraway waters, with the spirit, were found to be distinctly acid, reddening litmus paper and causing an effervescence with carbonated alkalies; all the others remained perfectly sound. They were again examined after a lapse of twelve months; the acidity had increased in the previous cases, while the same waters without the spirit, remained perfectly unchanged, and evidenced no signs of acidity. On examination after another twelve months they did not appear to have undergone any further alteration.

I need scarcely mention, that in selecting the specimens specified, the object was to try the general action of ordinary exposure to the atmosphere on waters varying in their characters and sources, as other samples might have been chosen which would doubtless have become acid as soon, or even sooner than the carraway and spearmint, as for instance, rose-water, elder-flower, orange-flower, peppermint, and penny-royal waters.

Another point in favour of these distilled waters keeping, was their having been prepared from their respective essential oils, and not from the herb, seed, or bark. It is stated that these waters are liable to become mucilaginous and sour when long kept, and that the small quantity of spirit is added to prevent this; from the foregoing experiments, however, it will be evidently seen to produce a directly contrary effect, and the formulæ of the Edinburgh and Dublin Pharmacopœias will be equally in error on this point.

It is curious that of the European Pharmacopœias, that I have looked into during this investigation, not one labours under this error, their instructions being simply to distil the materials with water.

On searching back through former editions of the London Pharmacopœia, to ascertain, if possible, whether the formulæ had always been the same, and if not, when this erroneous alteration had been effected, I found that in the Pharmacopœia of 1624 two classes of distilled waters are specified, entitled simple, and compound or spirituous; the former made without the addition of any spirit, either in the process or afterwards, the latter similar to the preparations entitled spirits of

the present day; after this date the error of adding small portions of spirit seems to have originated, and to have been regularly copied, with very little deviation, from edition to edition, down to the year 1836, the general directions being to distil a certain quantity of the water from a given weight of material, and then to add five ounces of proof spirit to each gallon, *that it may be preserved*, or rather I may say in many cases, to spoil it. In the edition of 1836, the proportion of spirit was increased to the formula that has been already given, and this was also the form prescribed in some of the various dispensatories about the middle of the eighteenth century.

On examining into the quantity of acid generated in the foregoing experiments, I found that half a pound of the carraway water required 4 grs. of dry carbonate of soda to effect perfect neutralization, which is equivalent to 4·45 grs. of real acetic acid. This acid was also isolated by distillation, and its identity proved by various tests.

We now pass on to the extemporaneous preparation of flavoured waters from their respective essential oils. The general formula given in the Pharmacopœia of 1836, in which it is introduced for the first time, is to triturate carefully together one drachm of the essential oil with one drachm of carbonate of magnesia, and afterwards with four pints of distilled water, and then strain. Now on examining the waters thus prepared, they are all found, without exception, to contain a notable quantity of magnesia, the proportions taken up seeming to vary with the various essential oils employed, all other circumstances remaining the same. Dr. Pereira, in his valuable 'Elements of Materia Medica,' vol. i. p. 258, speaks thus of these waters:—"The magnesia (carbonate of magnesia) effects the minute division of the oil. Moreover, when the oils possess acid properties, as the old oils of pimento, cloves and cinnamon, it probably serves to saturate them. Prepared in this way the medicated waters usually contain a minute portion of magnesia in solution: hence, by exposure to the air, they attract carbonic acid, and let fall flocculi of carbonate of magnesia. Moreover, the magnesia unfits them for the preparation of solutions of some of the metallic salts, as bichloride of mercury and nitrate of silver."

The method of examination adopted in the following experiments was to take a measured volume of the water, say 1000 grains, and evaporate it to dryness at a temperature not exceeding 212°, then to ascertain carefully the weight of the residue, redissolve it in dilute acid, and test the resulting solution. Magnesia in the form of carbonate was invariably found, together frequently, with resinous matter from the oil; this was

more especially the case where oils of considerable age had been employed. By this mode of operating, the results obtained range from 0·50 gr., in the 1000 gr. measures of the water, as in peppermint-water, to 1·20 gr. in dill and pimento waters; many others were tried, which ranged between these two points. It may perhaps be as well here to mention, that it was observed very soon after the application of the heat in evaporating, that flocculi of carbonate of magnesia invariably separated.

The general opinion has been that these waters were formed in consequence of the magnesia as a base favouring the union of the oil and water, and thus implying some combination of these materials; but I was led to believe, from various circumstances presenting themselves during these experiments, that this was not in any respect the true cause, and that the carbonate of magnesia acted simply as a mechanical subdivider of the oil, if I may be allowed the expression, so that the water acted as a solvent with greatly increased effect upon an enormously extended surface of the essential oil, as is the case in distillation, where the cohesive attraction of the molecules being overcome by the influence of heat, the vapours of the oil and water rise together, are mutually diffused and pass over into the refrigerator or worm to be condensed, and thus solution is to a certain extent effected. Under this impression the same experiments were repeated, substituting for the carbonate of magnesia the kaolin or porcelain clay of Cornwall, or finely-divided silica in the form of powdered flints, and with perfect success, the resulting medicated waters being perfectly colourless, transparent, and having a full flavour of their respective oils. On evaporation no residue was obtained, except in a few instances a small quantity of resinous matter, where, as before mentioned, oils had been used which had been made a long time: this amounted in the case of pimento water to 0·50 gr.

Two questions remain now to be settled arising out of the foregoing experiments; first, does the magnesia enter into combination with the acid oils existent in some of the essential oils used, as pimento, &c.? or, secondly, is the oil simply taken into solution by the distilled water? The fact of the carbonate of magnesia separating from the solution by the application of heat, and remaining always in the state of carbonate on evaporation to dryness at a temperature of 212° F., is a strong argument in opposition to the first of these questions, as I do not think the view taken by Dr. Pereira is possible, namely, that the magnesia of the carbonate of magnesia first combines with the acid of the oil, which as a consequence, implies the

evolution of its carbonic acid from its weaker affinity, and that then, by the absorption of carbonic acid from the atmosphere it is again deposited as carbonate of magnesia, thus making its affinity stronger; the second position being directly contradictory to the first.

On trying a repetition of the same experiments with the same materials, but omitting the essential oil, and going through precisely the same routine, I obtained from 0·50 to 0·70 gr. of carbonate of magnesia by evaporation as the average results of many trials; so that I consider from these data we may fairly conclude no combination of the magnesia and oily acids had taken place, but that it was simply a solution of the earthy carbonate in the distilled water; nevertheless, in many of the experiments, the presence of the different oils evidently affected the solvent power of the water and thus directly influenced the quantity of carbonate of magnesia taken up; and the resin existent in some of the old oils will account for the occasional increase of weight over this quantity, for it has been shown that this resin is soluble to some extent in water.

There can be no doubt, from the above experiments, that any insoluble substance in a fine state of division will answer the same purpose as the carbonate of magnesia much better, as, for instance, very fine porcelain clay, finely-divided silica, powdered glass, pumice-stone, &c. I am not aware how the use of carbonate of magnesia for the extemporaneous formation of these waters originated, except with the pharmaceutist as being a material generally at hand, and it is well known to have been the substance usually employed for this purpose for a great number of years, and was, I am informed, used by the perfumers to produce the same results long before its introduction for medicinal preparations.

February 3, 1845.—Robert Porrett, Esq., Treasurer, in the Chair.

Dr. Draper of New York, presented his work on the Chemistry of Plants to the Society's Library.

Messrs. Johnson and Cock exhibited Specimens of pure Palladium in its forged, rolled and finely laminated state, the former a mass weighing 100 ounces.

W. A. Gibbs, Esq., W. T. Rickard, Esq., and Robert Smith, Ph.D. were elected Members; and Mr. Joseph Cooper an Associate of the Society.

The following communication was then read:—

CXXIX. *On the Metamorphoses of Indigo. Production of Organic Bases which contain Chlorine and Bromine.* *By* Dr. August Wilhelm Hofmann, *Assistant in the Giessen Laboratory**.

THE changes which result from the action of various bodies upon indigo have for a series of years engaged the attention of chemists. It may be even said that this subject has been selected with preference for investigation; and when we consider the rich harvests already obtained by a great number of celebrated chemists, there would appear, at the first glance, scarcely anything to be gleaned. It is however the character of every rapidly-advancing science, that each discovery becomes the source of numerous others, and that the solution of every question gives rise to others which must in their turn be answered. It was thus that the further investigation of the products from the decomposition of indigo, which had been already so thoroughly studied in many points by Laurent and Erdmann, led to results which appeared to me worthy of publication.

Before proceeding, however, to the description of these results, it may be advantageous to make a few preliminary observations for the purpose of showing the reasons for which these investigations have been undertaken.

Among the various theories which have of late years claimed the attention of chemists, that of substitution occupies a very prominent place. It is not my intention to examine the numerous phases of this discussion, for the most part carried on in France, nor to consider minutely the various consequences which had their rise in this originally extremely simple question. The problem which forms the basis of the present investigation is a more general experimental establishment of a single substitution theorem.

If we examine carefully the origin of the theory of substitutions, we shall be able to trace it to the endeavour to predetermine, by means of certain laws experimentally established, the changes to be produced upon a body through the action of chlorine, bromine, oxygen, &c. In the course of such investigations it was however perceived, that in order to foretel these changes a complete knowledge of the constitution

* I have had the pleasure of witnessing the care and accuracy with which the author of this paper has proceeded in making his observations and establishing his facts.

It appears to me that he has produced a definite and irrefragable proof that the chemical character of a compound does not depend, as the electrochemical theory supposes, upon the *nature* of the elements it contains, but solely on the manner of their grouping.—Justus Liebig.

of the original body was necessary, and that this must be included in the argument. This discussion is not yet terminated, nor are we at present in a position to give an opinion as to its final result; this however is certain, that it has been the means of originating many excellent investigations, from which science has derived the greatest advantage.

It is now eight years since Laurent was led by a series of experiments to a peculiar mode of representing the action of chlorine on organic bodies, and among other views, of which we do not require here to speak, he laid down the following law:—

"In many organic compounds, by the action of chlorine, a certain number of equivalents of hydrogen are eliminated in the form of hydrochloric acid; the eliminated hydrogen being replaced by a like number of equivalents of chlorine, in such a manner, that the chemical character and the fundamental properties of the original compound are not sensibly altered. The chlorine molecules therefore must take the place of the hydrogen molecules, and play in the new compound the same part which was performed by the hydrogen molecules in the original."

The ideas of Laurent, which were opposed to the electrochemical theory, and to the views generally received at that time, found, as might be expected, but an indifferent reception from chemists at the period of their publication. His views were reproached with being supported by too small a number of facts; even his facts were assailed, and the author required all his dexterity and steady perseverance to defend himself against his powerful opponents. He repeated many of his former experiments, and added by further investigations new proofs to those already given. Since that time a mass of facts has been observed which unequivocally support the ideas of Laurent. The discovery of chloracetic acid by Dumas, the investigations of Regnault on the action of chlorine on the *Liqueur des Hollandais*, of Malaguti on the action of the same body on the compound æthers, the extended works of Laurent on the naphthaline and phenyle series, the researches of the same chemist and of Erdmann on indigo, have given so many instances in which any other view is inadmissible, that it would appear scarcely necessary to undertake still further investigations in its support.

On examining however more closely the bodies in which hydrogen has hitherto been replaced by chlorine in the way mentioned, it is found that they consist of indifferent bodies, or acids, or their compounds with æther. Up to the present time the theory of substitution remains unrepresented by a

large and important class of bodies. *No organic base* is known in which the hydrogen has been replaced by chlorine in the above-mentioned manner.* And yet it would be an argument of the greatest weight, were chlorine, an electro-negative element, to be introduced into a compound possessing electro-positive properties, without however changing its chemical character.

The above considerations induced me to undertake the following research.

The action of chemical agents in general upon the organic bases has been as yet but little studied. For the first accurate account of the special action of chlorine and bromine on these bodies, we are indebted to Pelletier †, who investigated the behaviour of strychnine toward chlorine, and at the same time communicated some details on the influence exercised by this body on quinine, cinchonine, brucine, morphine and narcotine. From his experiments he ascertained that chlorine withdrew from these bases hydrogen in the form of hydrochloric acid, and gave rise to neutral compounds difficult of solution in water, but soluble in alcohol. On submitting the crystalline product obtained from strychnine to analysis, the presence of chlorine in its composition was ascertained. Of the other bases, only quinine and cinchonine offered products of a somewhat crystalline structure. The physical properties of these substances however rendered their analysis so difficult, that we are still in the dark as to the relation which exists between them and the original compounds.

Lately Brande and Leben ‡ made some experiments on the action of chlorine on quinine, and described the various products—dalleiochine, rusiochine and melanochine, which all contain nitrogen but no chlorine. The properties of these bodies are not however well-defined, nor do their analyses bear the stamp of exactness, so that science has gained but little by their investigation. The same may be said of the researches of M. André § on the same subject.

All these details relate to solid crystalline bodies. As to

* By organic base, in the strict sense of the word, I understand here, with Liebig, that class of compound, azotized bodies, which possess all the properties of basic metallic oxides. The oxides of ethyle, methyle, &c., are not included, as the most common character of salts is wanting in their compounds, viz. the replacement of their acids by other acids, and their bases by other bases.

† *Journal de Pharmacie*, Avr. 1838, and Liebig's *Ann.*, Bd. xxix. S. 48.

‡ *Archiv der Pharmacie*, Bd. xvi. S. 257, and Liebig's *Ann.*, Bd. xxxii. S. 270.

§ *Ann. de Chem. et de Phys.*, t. lxxi. p. 195, and Liebig's *Ann.*, Bd. xxxii. S. 273.

volatile bases, all that we know is, that nicotine and coneine are decomposed by the action of chlorine, but no investigation has as yet been made of these products of decomposition.

On the other hand, there exist some accounts of the products obtained by chlorine and bromine from aniline, that artificial base which has of late been met with under so many different circumstances. These bodies crystallize, but they no longer possess the character of basic compounds.

I have myself communicated some observations on the action of chlorine on aniline, made during an investigation of the organic bases of coal-gas naphtha *. I could not at that time obtain a chlorinated basic product of decomposition from aniline. Besides a neutral compound, which was not produced in sufficient quantity for analysis, there was always formed as the chief product chlorindoptinic acid (chlorophenissic acid of Laurent), whose relation to aniline is shown by the following formula:

$$\underbrace{C_{12}H_5, NH_2}_{\text{Aniline.}} + 6\,Cl + 2\,HO = \underbrace{C_{12}\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}O + HO}_{\text{Chlorophenissic acid.}} + NH_3 + 3\,Cl\,H.$$

The action of bromine on aniline, investigated by Fritzsche†, is much less energetic. A simple substitution of bromine for hydrogen takes place, giving rise to the compound named by him bromaniloid,

$$\underbrace{C_{12}H_5, NH_2}_{\text{Aniline.}} + 6\,Br = \underbrace{C_{12}\left\{\begin{matrix}H_2\\Br_3\end{matrix}\right\}, NH_2}_{\text{Bromaniloid.}} + 3\,Br\,H.$$

But this compound too is no longer basic, but neutral, the positive properties of aniline being removed by the entrance of the electro-negative element into its composition. In these cases the action of chlorine and bromine has evidently gone too far for the aniline still to preserve its original character, and it remained therefore to try in some way to regulate the action of the above-named agents, so as to produce compounds in which only one equivalent of hydrogen was replaced, and which, like aniline, might possibly possess basic properties.

The remarkable facility with which the derived members of the phenyl family, viz. the chlorinated phenylic acid, as well as bromaniloid, crystallize, made it probable that the

* Liebig's *Annalen*, Bd. xlvii. S. 68, and Phil. Mag. vol. xxiv. p. 115.

† *Bullet. Scient. de St. Pétersb.*, 1843, t. i. p. 30, and Liebig's *Ann.*, Bd. xliv. S. 291.

desired compound would likewise be crystalline, by which the investigation would be rendered essentially easier. I resolved therefore to make my experiments in this direction.

Action of Chlorine on Aniline.

I began by carefully repeating my earlier experiments, but obtained exactly the same results.

As the action of chlorine on aniline immediately forms hydrochloric acid, I chose a solution of the base in this acid, and passed through it slowly a stream of the chlorine. After a few moments the fluid became violet, thickened and deposited a brown resinous matter, which fell to the bottom of the vessel. On submitting the whole fluid to distillation, a crystalline substance was deposited in the neck of the retort in the form of white needles, consisting of a mixture of two different bodies, which are easily separated by a second distillation with potash; an indifferent crystalline substance passes over, of which I shall immediately speak, and chlorophenissate of potash remains in the retort. The resinous matter submitted alone to distillation gave likewise a large quantity of chlorophenissic acid.

In no case could I obtain any other results than the above, however much I modified my experiments by employing a more or less diluted solution, and substituting a watery solution of chlorine instead of the gas. I soon found that the desired end could not be attained in this direct way, and had consequently to have recourse to an indirect method.

Aniline, originally discovered by Unverdorben* among the products of distillation of indigo, was afterwards produced by Fritzsche† on submitting anthranilic acid to the same process, and by Zinin‡ through the action of sulphuretted hydrogen on nitrobenzid. The idea occurred to me to try the action of chlorine on anthranilic acid, and should it so happen that in this way out of the anthranilic acid $C_{14}H_7NO_4$ by the substitution of chlorine, a compound, $C_{14}\left\{\begin{matrix}H_{7-n}\\Cl_n\end{matrix}\right\}NO_4$§, could be obtained possessing the properties of anthranilic acid, it was highly probable that by its distillation the desired base would be obtained. It was also probable that by the action of chlorine on nitrobenzide, $C_{12}H_5NO_4$, it would like-

* Poggend. *Ann.*, Bd. viii. S. 397.

† *Bul. Scient. de St. Pétersb.*, t. vii. No. 12, and t. viii., and Liebig's *Ann.*, Bd. xxxvi. p. 87.

‡ *Bul. Scient. de St. Pétersb.*, t. x. No. 18, and Liebig's *Ann.*, Bd. xliv. p. 283.

§ $n = 1$ or 2.

wise be transformed into a similar body, $C_{12}\left\{\begin{matrix}H_{5-n}\\Cl_n\end{matrix}\right\}NO_4$, and this body would require only to be treated with sulphuretted hydrogen to be changed into the desired compound.

Whilst occupied with the preparation of anthranilic acid, for the purpose of these experiments, another expedient offered itself, which, by changing completely the direction of my researches, led me quickly to the desired object.

It is well known that it is not necessary to employ pure anthranilic acid for the preparation of aniline, which may be obtained directly as a true product of oxidation by distilling indigo and hydrate of potash, as is shown in the following manner:—

$$\underbrace{C_{16}H_5NO_2}_{\text{Indigo.}} + 4\,HO = \underbrace{C_{12}H_7N}_{\text{Aniline.}} + 4\,CO_2 + 2\,H.$$

We may here take a short review of the substances obtained from indigo by other oxidizing means. By the action of nitric acid there is formed as the first product of oxidation a body named isatine, which was discovered by Laurent and Erdmann about the same time. This compound contains the elements of indigo, together with 2 equivalents of oxygen,

$$\underbrace{C_{16}H_5NO_2}_{\text{Indigo.}} + 2\,O = \underbrace{C_{16}H_5NO_4}_{\text{Isatine.}}$$

Aniline being, as was already remarked, a product of oxidation of indigo, it was in the highest degree probable, not to say certain, that it could also be obtained from isatine by fusing the latter with hydrate of potash. This question remained to be decided by experiment.

Action of Hydrate of Potash in fusion on Isatine*.

On pouring a solution of caustic potash on isatine in a tubulated retort, its colour becomes dark red, almost amounting to black, which, according to Laurent, is owing to a trans-

* All the isatine employed in the following experiments was prepared from commercial indigo, according to the method of Laurent, with common nitric acid; a very considerable quantity is thus obtained. In its preparation care must be taken not to employ too large a quantity of nitric acid, otherwise there is formed the indigotic acid discovered by Buff (also called aniline, and nitrosalicylic acid), which is at once recognised by the yellow colour of its crystals and the blood-red reaction with perchloride of iron. Neither must the indigo be mixed with too much water. After each addition of nitric acid effervescence should take place, which must be allowed to finish before adding a fresh quantity. Should this effervescence not take place, and a large quantity of nitric acid be added gradually to the boiling mixture, a most powerful reaction takes place at a certain point of concen-

itory combination of isatine with potash. By warming the potash-ley, a solution of the dark red crystals is made of the same colour, but so soon as the fluid comes to the boiling-point the colour changes to orange-yellow, and contains now isatinate of potash. At the beginning of the distillation pure water passes over, but at a certain concentration of the fluid, which can be hastened by the addition of pieces of solid hydrate of potash, a lively reaction takes place, and there distils over with the water a body in the form of oily drops, which possesses all the properties of aniline. During the operation, and particularly at the end, free hydrogen gas is evolved, and carbonate of potash remains in the retort. The following formula exhibits the decomposition:—

$$\underbrace{C_{16}H_5NO_4}_{\text{Isatine.}} + 4\,(KO, HO) = \underbrace{C_{12}H_7N}_{\text{Aniline.}} + 4\,(CO_2, KO) + 2\,H.$$

After this experiment, the preparation of the desired compounds was no longer a matter of difficulty. They must be obtained by the action of alkaline bases on chlorisatine and bichlorisatine.

The experiments about to be detailed will show how far this conclusion was correct, supported as it was by the complete analogy existing between isatine, chlorisatine and bromisatine.

Action of fused Hydrate of Potash on Chlorisatine.

On distilling chlorisatine* with a mixture of potash-ley and solid hydrate of potash, exactly the same phænomena present themselves as in the case of isatine, with the single difference,

tration of the fluid, and the mass flows over the largest vessels. The portions remaining contain generally only indigotic acid.

Isatine may be purified very easily in the following manner:—The crude product, still containing a quantity of resinous matter, is dissolved in potash-ley, and then carefully decomposed by the addition of hydrochloric acid so long as there is formed a black or brown precipitate. Should a small filtered portion possess a pure yellow colour, or the precipitate arising from the further addition of hydrochloric acid be of a pure lively red, the whole fluid is then to be separated by filtration from the resin and completely decomposed by hydrochloric acid. After washing with water, isatine obtained in this way is chemically pure.

* For the preparation of large quantities of chlorisatine I have always employed isatine, from the fact that chlorine in its action on indigo produces a mixture of chlorisatine and bichlorisatine, which can with difficulty be separated. Isatine is therefore much more convenient for this purpose. The change can be very much hastened by suspending isatine in boiling water, and directing a stream of chlorine through the fluid under the direct influence of the sun's rays. The transition is instantly recognised by the orange-yellow colour assumed by the crystals. As already stated by Erdmann (*Journal für Prakt. Chem.*, Bd. xxii. S. 272), not a trace of bichlorisatine is formed in this reaction, a fact also confirmed by my experiments.

that the oily fluid which distils over with the water condenses into a white crystalline mass in the neck of the retort, or, if this is too hot, in the cooled receiver. If the distillation is carefully conducted to prevent any of the fluid spirting over, the product collected in the receiver *does not react alkaline* so long as there remains a considerable quantity of water in the retort. When, however, the substance in the retort becomes nearly dry, a considerable quantity of ammonia, together with hydrogen, begins to be evolved, and the upper part of the retort becomes covered with a blue matter, which is sometimes carried over with the watery vapour into the receiver; at the same time the oily drops which have distilled over, from being colourless, now become brown and no longer solidify. At this period the distillation must be interrupted.

The crystalline substance which collects in the receiver can be purified with the greatest ease, by being thrown on a filter and washed with distilled water till all trace of ammonia is removed. To obtain it chemically pure, it is to be dissolved in boiling alcohol, from which it crystallizes in regular octahedrons. From the analysis it will be seen that this compound is aniline, in which one equivalent of hydrogen is replaced by one equivalent of chlorine. In short, it presents all the chemical characters and properties of aniline, and is like it a *base*. It may hence be denominated "chloraniline." If we employ the very excellent nomenclature of Laurent, who designates aniline by the name amaphenese (phenamide), then must the new chlorinated base be called amachlophenese.

A. *Chloraniline* (*Amachlophenese*).

a. Composition.

This substance was prepared and purified in the way above mentioned, and then dried in the air; in consequence of its containing chlorine, the combustion was made with chromate of lead.

I. 0·4495 grm. of substance gave 0·9210 grm. of carbonic acid and 0·1980 grm. of water.

II. 0·3220 grm. of substance gave 0·6670 grm. of carbonic acid and 0·1495 grm. of water.

III. 0·283 grm. of the substance well-mixed with powdered lime was placed in a tube, small pieces of lime added, and then submitted to a strong heat*. The residue, dissolved in

* Strong heat is necessary, as the substance is decomposed with difficulty. In a previous operation a small quantity distilled over undecomposed, which made the amount of chlorine too small.

0·3925 grm. of substance gave 0·400 grm. chloride of silver = 25·14 per cent. chlorine.

nitric acid and precipitated by nitrate of silver, gave 0·315 grm. of chloride of silver.

IV. The determination of the nitrogen was made in an atmosphere of carbonic acid. 0·597 grm. of substance burned with peroxide of copper gave, at 334‴ barom. and 11° centigrade, 58· cub. cent. of nitrogen. These numbers correspond to the following per-centage:—

	I.	II.	III.	IV.
Carbon* =	55·88	56·49		
Hydrogen =	4·89	5·15		
Chlorine =			27·45	
Nitrogen =				11·38

These numbers may be expressed in the following formula,— $C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N$, as is shown by comparison of the numbers calculated and found.

		Theory.	Per cent.	Mean of experiment.
12	Carbon =	900·00	56·43	56·18
6	Hydrogen =	75·00	4·70	5·02
1	Chlorine =	442·65	27·75	27·45
1	Nitrogen =	177·04	11·10	11·28
1 æq.	Chloraniline =	1594·69	100·00	99·95

To control this formula, I prepared the platinum double salt, which crystallized beautifully, and, after drying at the temperature of the air, analysed it. 0·5095 grm. of this salt, after combustion, left 0·1495 grm. = 29·34 per cent. of platinum; the atomic weight found from this = 1626·85; theoretical atomic weight = 1594·69. The agreement between the two is sufficiently near.

By adopting the formula $C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N$, which is completely established by the analyses of the different salts and the products of decomposition of the base, the formation of this body can be explained in the most satisfactory manner. It is, as was to be expected, completely analogous to the formation of aniline from isatine, as is shown by the following formulæ:—

$$\underbrace{C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}NO_4}_{\text{Chlorisatine.}}+4\,(KO,HO)=\underbrace{C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N}_{\text{Chloraniline.}}+4\,(CO_2KO)+2\,H.$$

I shall return afterwards to the origin of the ammonia in the last stage of the preparation.

b. Properties of Chloraniline.

I have already stated that this base is soluble in alcohol,

* Carbon = 75. Hydrogen = 12·5.

from which it crystallizes on cooling or by evaporation in regular octahedrons, in which the axes, as in the crystals of alum, have the planes of the cubes developed in a very high degree. I have obtained completely formed crystals, the axes of which were about a centimetre in length, and could be therefore submitted to the most exact crystallographic examination; they are not altered by exposure to the air. By rapidly cooling a boiling alcoholic solution of this base, it is deposited in the form of small, regular octahedrons, which present the most striking resemblance to codeine. The facility with which this body crystallizes is indeed remarkable; its solution yields by evaporation regular crystals even to the last drop.

This base is also extremely soluble in æther, pyro-acetic spirit, acetone, bisulphuret of carbon, fatty and æthereal oils. Water dissolves it but sparingly. By rapid cooling the boiling saturated solution becomes milky; but by proceeding slowly the base is deposited in well-defined small octahedrons, possessing the lustre of the diamond. By agitation with æther the base is withdrawn from the aqueous solution. Its odour is pleasant, somewhat like wine; its taste aromatic and burning. In both respects it cannot absolutely be distinguished from aniline. The crystals melt by heat. On making the experiment with a considerable quantity, the whole mass fused at a temperature of 64° to 65° cent. into a yellow oily liquid, which solidified on cooling into a mass of large octahedrons, the thermometer sinking at the same time to 57° cent. This base is in the highest degree volatile. The alcoholic solution cannot be evaporated without considerable loss. Even at common temperatures the crystals volatilize, as may be seen by the white vapours which arise on bringing near them a glass rod moistened with hydrochloric acid. With water the base can easily be distilled. In an experiment to distil it alone, made with a small quantity, I always obtained, besides the oily drops, the blue product of decomposition which I have already stated is formed in the preparation of the base. This decomposition prevents the determination of the boiling-point, which at all events lies above 200° cent. The vapour of the base burns with a brilliant smoky flame, possessing the green-coloured border peculiar to organic compounds containing chlorine.

It is heavier than water, and neither alone nor in solution does it exhibit the least reaction on turmeric or reddened litmus paper. Dahlia paper is coloured of a feeble green.

From what has been stated, it appears that chloraniline almost completely corresponds in its physical properties to aniline. The chief difference is that aniline is fluid at common temperatures, whilst the chlorinated compound is solid.

In their relation to other bodies, both compounds also agree, but to a more limited extent. The intense yellow colour given to pine-wood and the pith of the elder tree by acid solutions of aniline, is also produced by the salts of the chlorinated compound. On the other hand, the characteristic violet colour communicated to aniline by chloride of lime, is not exhibited by the compound derived from it; a solution of this reagent by mixture with this body assuming only a slight shade of violet. The solution of the salts takes the same colour, which however rapidly passes into orange. Neither is a cold or hot watery solution of the base nor of its salts altered by chromic acid, whilst aniline under the same circumstances gives rise to dark or greenish-blue products. On adding chromic acid to the crystals of the chlorinated base, they become brown and resinify. A mixture of these crystals with solid chromic acid inflames at the fusing-point of the base.

With regard to its relation to other reagents, I have to remark the following:—Peroxide of iron is not precipitated by the watery or alcoholic solution of the base. In both cases the fluid becomes green, from a partial reduction of the persalt of iron. By employing a watery solution of the base or crystals of it, a violet product of oxidation separates at the boiling-point, which is soluble in alcohol. No change is produced in protosalts of iron, nor in sulphates of alumina or of zinc, even by boiling them with the crystals. These oxides, however, are precipitated by aniline, from which it is evident that by the entrance of chlorine into its composition, its basic properties are somewhat enfeebled. Sulphate of copper is not precipitated by a watery solution of the base, but on adding some of its crystals to a boiling copper solution, the latter is immediately decolorized, and then deposits a mass of crystals of a bronze colour, which are insoluble in water, but are partially dissolved in boiling alcohol, from which on cooling they crystallize in the form of scales. It appears to be a double salt of sulphate of copper and of the chlorinated base. Similar double salts are produced with the perchlorides of mercury, platinum and palladium; the first of these being white, the latter two of a splendid orange-yellow colour. The precipitate from a gold solution is reddish brown. Tincture of galls is not changed by a cold solution of the base, but on adding a hot saturated solution, a yellow flocky precipitate is produced on cooling. Other chemical reagents are not affected by its watery solution.

c. Compounds of Chloraniline.

The extraordinary facility of crystallizing which distin-

guishes the chlorinated base are found in nearly all its compounds with acids; most of them are precipitated as a crystalline mass by mixing its alcoholic solution with the respective acids. By recrystallization from boiling water or alcohol they are obtained quite pure; with the exception of the platinum and palladium double salts they are white, but the larger crystals have generally a shade of yellow. An excess of acid imparts to them a violet tint. An elevation of temperature is observed in the formation of these compounds, &c.; they possess the true character of salts by their capability of undergoing double decomposition. As this base has no alkaline reaction, all its salts, as a consequence, possess acid properties. A large excess of the base can be heated to fusion under dilute hydrochloric acid without removing the acid properties of the supernatant fluid.

The salts are decomposed with the greatest ease by the caustic and carbonated alkalies; in the latter case with evolution of the carbonic acid, which does not unite with the base. The base itself separates in the form of a crystalline mass. The same decomposition is also produced by hydrochlorate of ammonia in solution. By heating it, however, in a tube with hydrochlorate of ammonia, evolution of ammonia takes place, and the hydrochlorate of the base is deposited on the cool portion of the tube.

Its capacity of saturation is the same as that of aniline, although the atom of the latter is lower than that of the former by the difference of the equivalents of chlorine and hydrogen ($442{\cdot}65 - 12{\cdot}50 = 430{\cdot}15$).

The constitution of the salts in no respect differs from those of ammonia. They unite directly with the hydracids, and with the oxacids by the addition of an equivalent of water.

Sulphate of Chloraniline.—SO_3, $C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N + HO$.

The alcoholic solution of chloraniline forms, by the addition of a few drops of sulphuric acid, a white crystalline mass, which by re-solution in boiling water separates on cooling as a confused mass of tabular crystals. From boiling alcohol, in which the salt is less soluble, it crystallizes in stellated tufts of fine silvery needles. Their crystalline form cannot however be determined. Even by slow evaporation of the alcoholic, as well as the watery solution, over sulphuric acid, I was unable to obtain large crystals. The salt is not volatile. By heating, a portion of the base escapes unchanged, while the remainder becomes black and evolves sulphurous acid.

Only one combustion of this salt was made. 0·3445 grm.

gave 0·5290 grm. of carbonic acid and 0·1365 grm. of water. These numbers correspond in the 100 parts to

Carbon . . . . = 41·87
Hydrogen . . . = 4·40

The formula is SO_3, $C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N + HO$, which gives

Carbon . . . . = 40·75
Hydrogen . . . = 3·96

The excess of carbon arises from the formation of a small quantity of deutoxide of nitrogen, which almost always takes place in the combustion of such bodies, if a very considerable quantity of copper turnings is not placed at the fore part of the combustion tube. I did not think it necessary to repeat this analysis, as it was only intended to give a view of the constitution of the salt.

Binoxalate of Chloraniline, $2C_2O_3$, $C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N + HO + 2$ aq.

By dissolving crystals of chloraniline in a warm watery solution of oxalic acid, a salt separates on cooling, which by re-crystallization from hot water is obtained in long needles like saltpetre. These consist of closely agglomerated prisms, and hence could not be used for the determination of the crystalline form. The salt is difficultly soluble in cold water and alcohol. It is without smell, but possesses a sweetish burning taste. Its solution becomes coloured on exposure to the air, and deposits gradually a red powder. The following results were obtained on burning this compound with chromate of lead:—0·4475 grm. gave 0·6990 grm. of carbonic acid and 0·171 grm. of water, or in the 100 parts,

Carbon . . . . = 42·59
Hydrogen . . . = 4·24

These numbers give the following formula:—

$$2C_2O_3,\ C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N + HO + 2\text{ aq.}$$

			Theory.		Found.
16 equiv.	of	Carbon . .	= 1200·00	42·37	42·59
9	...	Hydrogen .	= 112·50	3·97	4·24
1	...	Chlorine .	= 442·65		
1	...	Nitrogen .	= 177·04		
9	...	Oxygen . .	= 900·00		
			2832·19		

To control this formula I determined the amount of oxalic acid in the salt. 0·339 grm. of the salt, saturated with am-

monia and precipitated by chloride of calcium, gave, after heating to redness, 0·153 grm. of carbonate of lime, which corresponds to 32·18 per cent. of anhydrous oxalic acid.

			Theory.		Found.
2 equiv. of	Oxalic acid	=	900·00	31·77	32·18
1 ...	Base . .	=	1594·69	56·30	
3 ...	Water .	=	337·50	11·93	
			2832·19	100·00	

The above salt corresponds in its constitution to the binoxalate of ammonia and to Zinin's binoxalate of naphtalidan. As a neutral oxalate of aniline is known, I thought I might obtain the neutral salt of the chlorinated base by mixing its watery solution with oxalic acid in such a way as to leave the former in great excess. From this mixture, on cooling, separated needle-form crystals, which were washed and recrystallized. The combustion with chromate of lead gave from 0·4215 grm., dried at the temperature of the air, 0·6565 grm. of carbonic acid and 0·1490 grm. of water, corresponding in the 100 parts to

Carbon . . . . . 42·69
Hydrogen . . . . 3·92

hence proving that even under the conditions above-mentioned an acid salt had been formed.

An acid oxalate of aniline has not as yet been analysed. I endeavoured to form such a salt by saturating aniline with a large excess of oxalic acid. The precipitate formed was washed and frequently recrystallized from water. The needles obtained in this way possessed great similarity to the acid salt of the chlorinated base; they were, however, neutral oxalate of aniline, as was proved by the combustion. 0·3660 grm. of the salt gave 0·8188 grm. of carbonic acid and 0·2088 grm. of water. In 100 parts,

Carbon . . . . . 61·01
Hydrogen . . . . 6·33

The formula is $C_2 O_3$, $C_{12} H_7 N + HO$, which gives

Carbon . . . . . 60·79
Hydrogen . . . . 5·79

Nitrate of chloraniline is obtained by simply heating the base in dilute nitric acid. On cooling, the fluid becomes filled with tabular crystals, which generally possess a reddish tint. The salt is tolerably soluble in both alcohol and water. By heat it fuses into a dark mass, which forms with alcohol a beautiful rich blue solution, from which the nitrate, partly unchanged, again separates. I could not sublime this compound.

Phosphate of Chloraniline.

A solution of the base in alcohol forms, with phosphoric acid, a thick mass of crystalline plates, which are tolerably soluble in alcohol and water. I have not made any further investigation of this salt.

Hydrochlorate of Chloraniline, $ClH, C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N$.

Forms large, colourless, transparent crystals, which are obtained on cooling from a hot saturated solution of the base in hydrochloric acid. By redissolving in water and slowly evaporating the dilute solution over sulphuric acid, large well-formed crystals are produced. In describing the corresponding bromine compound I shall speak more of their crystalline form. They remain unchanged on exposure to the air, but become white and opake by the application of heat. If the heat be carefully applied they can be sublimed in a tube like sal-ammoniac; by sudden elevation of the temperature, however, the salt is decomposed with evolution of a violet-blue vapour.

The analysis of the crystals, dried at the temperature of the air, gave the following results:—0·3155 grm. of the salt precipitated with nitrate of silver gave 0·271 grm. of chloride of silver, corresponding to 22·10 per cent. of hydrochloric acid, which leads to the formula $ClH, C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N$.

	Theory.		Experiment.
1 eq. Chloraniline . .	= 1594·69	77·80	77·90
1 eq. Hydrochloric acid	= 455·15	22·20	22·10
1 eq. Hydrochlorate of chloraniline .	= 2049·84	100·	100·

Chloraniline and Bichloride of Platinum.

$$ClH, C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N + Cl_2Pt.$$

A solution of chloraniline in hydrochloric acid is precipitated of an orange-yellow colour by bichloride of platinum. If the two solutions are mixed hot, the whole fluid on cooling becomes a mass of crystalline plates. This double salt is very soluble in water, spirits of wine, and even in a mixture of alcohol and æther. To obtain it pure it is to be washed with cold water till the fluid, which continues to possess an evident acid reaction, passes colourless. On exposing the moist salt to the light, it becomes of a violet colour on the surface, which arises probably from the oxidizing ac-

tion of the bichloride of platinum by the presence of water. Evaporated over sulphuric acid this salt forms little rounded lumps, which exhibit no facets. On burning with chromate of lead the following result was obtained:—

0·463 grm. of the platinum double salt gave 0·374 grm. of carbonic acid and 0·096 grm. of water; corresponding in the 100 parts to Carbon . . . 22·03
Hydrogen . . 2·30

These numbers, with the determination of the platinum already mentioned, give the following formula:—

$$Cl\,H,\,C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N + Cl_2\,Pt.$$

		Theory.		Experiment.
12 equiv.	Carbon . .	= 900·00	21·53	22·03
7 ...	Hydrogen .	= 87·50	2·09	2·30
4 ...	Chlorine . .	= 1770·61	42·47	
1 ...	Nitrogen .	= 177·04	4·24	
1 ...	Platinum .	= 1233·50	29·46	29·34
1 eq. of the double salt		= 4168·65		

Bichloride of Mercury and Chloraniline.

This salt can be obtained in beautiful fine needles by pouring an alcoholic solution of the base into a hot solution of corrosive sublimate. At first the fluid remains clear, but after a few moments begins to get turbid, and gradually thickens completely into a mass of needle-form crystals of the double salt. I have not investigated other salts of the base. I may, however, mention a very beautiful double salt formed with chloride of zinc: by the mixture of the two solutions the fluid remains at first clear, but after a short time becomes a mass of silvery crystals.

d. Products of the Decomposition of Chloraniline.

I have not as yet so fully studied the products of the decomposition of this base as they deserve. Indeed it appears to suffer in contact with other bodies the same changes as aniline. The presence of the chlorine seems to have no influence in the processes of transformation, but passes over into the new products just as the hydrogen of aniline which it has replaced. I intend to investigate this subject more fully, and shall mention here only those phænomena which came under my observation during the course of the present inquiry.

Action of the Oxygenated Compounds of Chlorine on Chloraniline.

On adding crystals of this substance to a mixture of chlo-

rate of potash and hydrochloric acid, the fluid at first becomes violet-red and then gradually turbid and brown. The action is much hastened by the addition of alcohol, by which at the same time, however, acetic æther is formed. By long-continued action the fluid becomes again colourless, and a yellow crystalline matter is obtained, which can be easily purified by washing with alcohol and æther, in which it is but little soluble.

This substance crystallizes from boiling alcohol on cooling in small yellow plates. By slowly heating it sublimes without residue in the form of beautiful glittering scales of a golden colour. Potash forms with it a blood-red solution, from which, after some time, ruby-red prisms separate, which become of a vermilion colour by moistening with hydrochloric acid, and after removal of the acid dissolve in pure water with a beautiful violet colour. All these phænomena characterize in an undoubted manner the chloranil discovered by Erdmann in his investigations on indigo, a substance which, as I proved* a few months ago, is formed also in many other processes.

If the action of the oxidizing mixture on the chloraniline is not allowed to go so far, the chloranil is obtained mixed with a viscid matter, which is very soluble in alcohol and æther. On evaporating off the æther and submitting the resinous residue to distillation, oily drops pass over and crystallize in the neck of the retort. They possess the characteristic smell and peculiar reactions which distinguish the chlorophenissic or chlorophenussic acid of Laurent, namely the forming a violet precipitate with sulphate of copper, and a citron yellow with nitrate of silver.

The formation of all these bodies is easily explained. The nitrogen with a portion of the hydrogen forms ammonia, the presence of which can be proved in the mother-liquor. The remaining hydrogen is entirely or partially replaced by chlorine, chlorine and oxygen being called into action in the mixture of hydrochloric acid and chlorate of potash, whilst at the same time oxygen enters into the compound.

The following formulæ show the reactions:—

$$\underbrace{C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N}_{\text{Chloraniline.}} + 5Cl + 4O = \underbrace{C_{12}Cl_4O_4}_{\text{Chloranil.}} + NH_3 + 3Cl\,H.$$

$$\underbrace{C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N}_{\text{Chloraniline.}} + 2HO + 4Cl = \underbrace{C_{12}\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}O, HO}_{\text{Chlorophenissic acid.}} + NH_3 + 2Cl\,H.$$

$$\underbrace{C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N}_{\text{Chloraniline.}} + 2HO + 8Cl = \underbrace{Cl_{12}Cl_5O, HO}_{\text{Chlorophenussic acid.}} + NH_3 + 4Cl\,H.$$

* Mem. Chem. Soc. vol. ii. p. 227.

Chloraniline thus gives, under the same circumstances, as was to be expected, the same products of decomposition as aniline.

Action of Chlorine on Chloraniline.

At the commencement of this memoir are given the facts observed by the action of chlorine on aniline. The chlorinated base suffers precisely the same decompositions. There are formed chlorophenissic acid and a neutral body, the latter being trichloraniline, $C_{12}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right\}N$. I shall return immediately to its preparation and its properties.

Action of Bromine on Chloraniline.

By mixing aniline with bromine, heat and hydrobromic acid are disengaged, and there is formed Fritzsche's bromaniloid (tribromaniline), $C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N$. The chlorinated base suffers the same decomposition with brom ne. The product differs from the foregoing only in containing chlorine. It has the following composition, as we shall see afterwards:—

$$C_{12}\left\{\begin{matrix}H_4\\Cl\\Br_2\end{matrix}\right\}N.$$

Action of Nitric Acid on Chloraniline.

The decomposition produced in the chlorinated base by nitric acid I have unfortunately as yet but incompletely studied, although this point would have been of particular interest to have cleared up satisfactorily.

By the action of nitric acid aniline is transformed into carbazotic acid. It is in the highest degree probable that by the action of this oxidizing agent on chloraniline picric acid is formed, in which 1 equiv. of hydrogen is replaced by 1 of chlorine, having the formula $C_{12}\left\{\begin{matrix}H\\Cl\\3NO_4\end{matrix}\right\}O + HO$. By adding concentrated nitric acid to the chlorinated base, a lively reaction takes place, the fluid remains for some time boiling without the application of external heat, evolves nitrous acid, and becomes dark red, and finally black and opake. By continued action it becomes again transparent, and by allowing the scarlet red fluid to cool there sometimes separate golden yellow needles, which are very similar to the nitropicric acid. No trace of chlorine can be then detected in the fluid by nitrate of silver.

I made a great number of experiments to discover under what conditions this body was formed, but as yet I have not been able to produce it at will. In most cases I obtained instead a resinous body, which was precipitated in the form of yellow flakes from the nitric acid by addition of water, and which possessed the same property as nitropicric acid of tinging the skin. This substance is soluble in alcohol and æther, but cannot be obtained from the solution in a crystalline form. It is also soluble in the alkalies and ammonia, and is again precipitated by acids. By boiling the ammoniacal solution till the excess of ammonia is removed, and then adding nitrate of silver, a reddish-yellow precipitate is formed, which I was able to obtain only on one occasion in a crystalline form. My substance was, however, all expended ere I could discover a good method of preparation. Further experiments are necessary to decide the correctness of the forementioned hypothesis.

Action of Anhydrous Baryta and Lime on Chloraniline.

Though the examples are numerous in which the hydrogen of organic bodies has been replaced by chlorine, yet chemists have seldom been able to expel, without complete disorganization of the body, the assumed chlorine and refix the hydrogen in its old position. Indeed I know of no other instance than that of the regeneration of acetic acid from the chloracetic, performed by Melsens, by the employment of potassium amalgam.

From chloraniline aniline can likewise be reproduced. If a few crystals be placed in the end of a combustion-tube and lime in small pieces be laid before it, on heating the lime to a low red heat, there distils over a yellow oil which no longer becomes crystalline, and by all its reactions is at once recognised as aniline. At the same time a considerable quantity of ammonia is evolved, and there remains in the tube chloride of calcium and a large quantity of carbonaceous matter.

The regeneration of aniline is, as must be at once seen, essentially different from that of the acetic acid. In the reproduction of acetic acid from the chloracetic the hydrogen assumed is derived from the water present, its oxygen serving to oxidize the potassium; in the case of aniline the requisite hydrogen is furnished by that substance itself, which must consequently be partly decomposed. One equivalent of the chlorinated base contains just sufficient hydrogen to convert its nitrogen into ammonia, its own chlorine and that of another equivalent of base into hydrochloric acid, and finally, to furnish the required equivalent of hydrogen to the now regene-

rated aniline. Its carbon must, therefore, be completely separated. The following formula exhibits this change:—

$$\underbrace{2C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N}_{\text{Chloraniline.}} + 2CaO = \left\{\begin{matrix}C_{12}N_7N + C_{12} + 2Cl\,Ca +\\ 2HO + NH_3.\end{matrix}\right.$$

This decomposition gives the key to some phænomena of which I have already made mention in the preparation of chloraniline.

I mentioned that in the last stage of the distillation, so soon as the mass in the retort commences to become dry, evolution of ammonia takes place, and aniline at the same time distils over. This reaction evidently depends on a transformation similar to that just mentioned. The vapours of the chlorinated base which deposit on the cooler parts of the apparatus meet with hot potash on the sides of the retort, and are decomposed into aniline, ammonia, and hydrochloric acid.

By carefully mixing a small portion of very pure chlorisatine with caustic baryta and slowly heating, a product of distillation was obtained which did not exhibit the slightest alkaline reaction, whilst, in the heated residue, not a trace of chlorine could be detected. All the nitrogen and chlorine of the chlorisatine had consequently distilled over in the form of chloraniline.

Action of Potassium on Chloraniline.

The decomposition experienced by the chlorinated base when its vapour is passed over fused potassium offers no great peculiarity. The potassium becomes incandescent and is converted into chloride and cyanide. A large quantity of carbon is also deposited.

Action of the fused Hydrate of Potash on Dichlorisatine.

B. *Dichloraniline* (*Amachlophenise*).

Erdmann has proved by direct experiment that chlorisatine cannot be converted into dichlorisatine by the further action of chlorine on this substance suspended in water. I have had frequent opportunities of convincing myself likewise of this fact. If an alcoholic solution be employed the decomposition proceeds too far, and products of oxidation are obtained, viz. chloranil, chlorophenussic acid, &c., which no longer belong to the isatine series.

I endeavoured to prepare dichlorisatine by dissolving isatine or chlorisatine in potash and passing a stream of chlorine

gas through the solution of isatinate or chlorisatinate of potash. The result was however unfavourable. No dichlorisatine was formed, but in its stead a tarry matter, which floated on the surface of the fluid; it was insoluble in water but soluble in alcohol. I was equally unsuccessful in dissolving chlorisatine in nitric acid and adding to the solution a few drops of hydrochloric acid. A violent reaction ensued, and the decomposition had evidently proceeded too far. There remained, therefore, only to fall back upon the method employed by Erdmann to prepare this substance, and of which Laurent had also made use in his investigation. It consists in treating indigo directly with chlorine. In this process, under every circumstance, there is formed a mixture of chlorisatine and dichlorisatine, the quantity of the latter, according to Erdmann, greatly preponderating. Chlorisatine and dichlorisatine can only be separated from each other by crystallization with extreme difficulty. The amount I had obtained was too small to think of trying to separate them in this way; I therefore at once submitted the mixture with hydrate of potash to distillation.

The distilled product contained, besides chloraniline, another basic substance, collecting on the surface of the fluid, which crystallized in long prisms. This substance was manifestly nothing but dichlorisatine, $C_{12}\left\{\begin{matrix}H_5\\Cl_2\end{matrix}\right\}N$. The crystals which could be picked out of the fluid unfortunately were not sufficient in amount for a combustion. As I have, however, more completely studied the corresponding bromine compound, which is much more easily prepared, I considered it useless to occupy myself longer with this substance.

C. *Trichloraniline* (*Amachlophenose*). $C_{12}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right\}N$.

Isatine, in which 3 equivalents of hydrogen are replaced by three of chlorine, is as yet not known. The preparation of trichloraniline could not hence be made by persevering in the method hitherto used. It is however procured, as above mentioned, by the direct action of chlorine on aniline or the chlorinated base.

By submitting to distillation with hydrate of potash the crude product of the action of chlorine on these two bodies, which contains a mixture of chlorophenissic acid and trichloraniline, the first remains in the retort in combination with potash, while the latter passes over into the receiver with the watery vapour, and collects on the surface of the liquid in long needles. As this substance is very volatile, a cooling apparatus must always be employed in this distillation.

Trichloraniline is very little soluble in water, but dissolves readily in alcohol and æther. The solution has a neutral reaction. It does not unite with bases or acids, and can be distilled unchanged from water containing either acid or alkali.

This substance is obtained only in small quantities. My whole amount, after the qualitative determination of chlorine and nitrogen, was just sufficient for one analysis, which unfortunately did not turn out very good, but could not be repeated from the fact already mentioned. By burning with chromate of lead the following results were obtained :—

0·3020 grm. of the substance gave 0·4170 grm. of carbonic acid, 0·0665 grm. of water. In the 100 parts—

Carbon . . .	37·65
Hydrogen . .	2·44

The formula is $C_{12}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right\}N$. The theoretical constitution is

12 equiv.	Carbon	=	900·00	36·66
4 ...	Hydrogen	=	50·00	2·03
3 ...	Chlorine	=	1327·95	54·09
1 ...	Nitrogen	=	177·04	7·22
			2454·99	100·

It may perhaps appear bold to give an opinion as to the constitution of this body from a single determination of its carbon and hydrogen, which, besides, does not agree very well with the theory. When however we consider the complete analogy in the mode of formation of tribromaniline and chlorodibromaniline, to which I shall afterwards return, and the exact resemblance in the properties of these bodies, less doubt may perhaps be entertained.

It appeared to me also to be worth the trouble of endeavouring to form a base which contained bromine as well as chlorine. Such a body could with ease be obtained, were it possible to form a chlorobromisatine, $C_{16}\left\{\begin{matrix}H_3\\Cl\\Br\end{matrix}\right\}NO_4$. Distilled with hydrate of potash, this compound would yield chlorobrominated aniline, $C_{12}\left\{\begin{matrix}H_5\\Cl\\Br\end{matrix}\right\}N$. For this purpose, I poured on chlorisatine in a retort an excess of bromine, allowed the whole to remain for twelve hours, and then heated it in a water-bath to the boiling-point, until the excess of bromine was distilled off. The red crystals were separated by filtration, washed and crystallized from hot alcohol.

The prismatic crystals thus obtained produced on burning with chromate of lead the following result:—

0·2955 grm. gave 0·5697 grm. of carbonic acid and 0·0695 grm. of water; corresponding in the 100 parts to

Carbon . . .	52·57
Hydrogen . .	2·61

This substance was consequently nothing but pure undecomposed chlorisatine, which contains in 100 parts—

Carbon . . .	52·88
Hydrogen . .	2·25

This compound, $C_{16}\left\{\begin{matrix}H_3\\Cl\\Br\end{matrix}\right\}NO_4$, would have contained

Carbon . . .	36·90
Hydrogen . .	1·15

The small quantity of hydrobromic acid observed in this action of bromine on chlorisatine may have arisen from a small admixture of isatine, which would be converted into bromisatine. By continued action of bromine in sunshine, perhaps another result might be obtained.

D. *Chlorodibromaniline* (*Amachlobrophenose*). $C_{12}\left\{\begin{matrix}H_4\\Cl\\Br_2\end{matrix}\right\}N$.

It has been already stated that aniline is decomposed with facility by bromine. On adding bromine water to the solution of a salt of chloraniline, a white precipitate takes place, which dissolves in boiling alcohol, producing a slight violet colour, and crystallizes on cooling in needles. The same compound can be obtained by the direct action of bromine on chloraniline. On adding bromine to the crystals of the latter, a very violent reaction takes place, with great elevation of temperature and evolution of hydrobromic acid, the mixture at the same time assuming a violet colour. Bromine is to be added till the mass on being fused no longer absorbs any more. The crystalline product is then to be allowed to cool, and well-washed till all trace of hydrobromic acid is removed. By recrystallization from alcohol, white crystals are obtained, which have generally a shade of red.

Fritzsche, as is known, has discovered that by the action of bromine on aniline there is formed a body, $C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N$, which he called bromaniloid. From this decomposition we can already foresee the composition of the product which I obtained by the action of bromine on the chlorinated base. This must stand in the same relation to the bromaniloid that

the chlorinated base does to aniline, and consequently would be expressed by the formula $C_{12}\left\{\begin{matrix}H_4\\Cl\\Br_2\end{matrix}\right\}N$.

This conclusion is completely confirmed by the analysis.

The combustion with chromate of lead gave the following results:—

0·520 grm. crystals, dried at the temperature of the air, gave 0·485 grm. of carbonic acid and 0·070 grm. of water; corresponding in the 100 parts to

Carbon . . .	25·43
Hydrogen . .	1·52

which will give the calculated composition,—

			Theory.		Experiment.
12 equiv.	Carbon . . .	=	900·00	25·52	25·43
4 ...	Hydrogen . .	=	50·00	1·41	1·52
1 ...	Chlorine . . .	=	442·65		
2 ...	Bromine . . .	=	1956·61		
1 ...	Nitrogen . . .	=	177·04		
1 ...	Chlorodibromaniline	=	3526·30		

The formula of this compound is $C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N$, and it contains

Carbon	= 22·15
Hydrogen	= 1·22

This body is completely insoluble in water, but soluble in alcohol and æther. It melts under water into a brown oily fluid, which can be distilled over with the vapour of water; it crystallizes in shining needles on the sides of the receiver. Chlorodibromaniline, like the trichloraniline, no longer possesses basic properties. It is soluble in boiling hydrochloric acid, out of which however the greater part again recrystallizes unchanged on cooling. The portion soluble in hydrochloric acid at the ordinary temperature is precipitated by the addition of water. Strong sulphuric acid likewise forms with it a solution of a violet colour, from which it is also precipitated by the addition of water. Neither potash nor ammonia decomposes this substance, which by heat is slightly soluble in these fluids without the least change. It does not combine with bichloride of platinum or mercury, or with oxide of lead. Concentrated nitric acid decomposes the chlorodibromaniline.

Action of fused Hydrate of Potash on Bromisatine.

It was evidently to be expected that the brominated isatine would yield the same results as the chlorisatine. This was

confirmed by experiment. Bromisatine has been as yet but little studied. Erdmann* obtained it in very small quantities by the direct action of bromine on indigo. Laurent did not prepare this subtance; by the action of bromine on isatine he obtained immediately dibromisatine (bromisatinese). The first compound can however easily be formed by employing a solution of bromine in water instead of anhydrous bromine. In two experiments I obtained bromisatine alone, as is shown by the following analysis. The compound is dissolved out by boiling spirits of wine, washed with water to remove all trace of hydrobromic acid, and recrystallized in boiling alcohol, from which it separates in shining prisms

The following result was obtained on combusion with chromate of lead:—

I. 0·3270 grm. of bromisatine gave 0·5090 grm. of carbonic acid and 0·0625 grm. of water.

II. 0·3955 grm. of bromisatine gave 0·6165 grm. of carbonic acid and 0·0750 grm. of water.

These numbers give the following per-centages, which are placed in apposition with the calculated quantities:—

		Theory.		Experiment.	
				I.	II.
16 equiv.	Carbon .	= 1200·0	42·41	42·45	42·51
4 ...	Hydrogen	= 50·0	1·78	2·12	2·10
1 ...	Bromine .	= 978·31			
1 ...	Nitrogen .	= 177·04			
4 ...	Oxygen .	= 400·00			
1 ...	Bromisatine	= 2805·35			

The properties of this body, which I obtained in large quantities, agree completely with those of chlorisatine, to which on this account I refer in the memoirs of Erdmann and Laurent.

On submitting bromisatine to distillation with fused hydrate of potash, exactly the same phænomena are observed as those I have already described in the same process with chlorisatine, and there distils over a new base containing bromine.

E. *Bromaniline* (*Amabrophenese*).

a. Composition.

The purification of the crude product of distillation is made with the same ease as in the case of the corresponding chlorine compound. The analogy in the mode of formation of the two left no uncertainty as to the composition of bromani-

* *Journal für Prakt. Chem.*, Bd. xix. S. 358.

line. To banish all doubt, however, I determined the carbon and hydrogen.

The following results were obtained on combustion with chromate of lead:—

0·4152 grm. of the brominated base gave 0·6463 grm. of carbonic acid and 0·1405 grm. of water. The corresponding numbers in the 100 parts found and calculated are as follows:—

12 equiv.	Carbon	=	900·00	42·24	42·45
6 ...	Hydrogen	=	75·00	3·52	3·75
1 ...	Bromine	=	978·31		
1 ...	Nitrogen	=	177·04		
1 ...	Bromaniline	=	2130·35		

The formula is $C_{12}\left\{\begin{matrix}H_6\\Br\end{matrix}\right\}N$. To control this formula the platinum double salt was prepared and analysed: 0·462 grm. gave 0·161 grm. = 26·19 per cent of platinum.

Atomic weight calculated from this . .	2125·80
Theoretical atomic weight	2130·35

This agreement is sufficiently close.

b. Properties of Bromaniline.

The bromine base resembles in so high a degree the chlorine, that I shall have little to say on this point. It crystallizes also with the same facility in large, colourless, regular octahedrons, which in appearance can be as little distinguished from the chlorine base as the bromide from the chloride of potassium. The same similarity extends to its smell, taste and other properties. Its point of fusion, however, lies somewhat lower than that of the chlorine compound. At 50° cent. it melts to a violet oily liquid. On solidifying, the thermometer descends to 46° cent.

The salts of this base, like those of aniline and chloraniline, impart a yellow colour to pine-wood, and its watery solution communicates to chloride of lime a violet tint, much weaker than that caused by aniline, but, on the other hand, much stronger than that produced by chloraniline.

c. Compounds of Bromisatine.

What I have said with regard to the formation and preparation of the compounds of the chlorine base applies for the most part to the salts of the corresponding bromine base. I have only investigated some of these fully.

Oxalate of Bromaniline. $C_2O_3, C_{12}\left\{\begin{matrix}H_6\\Br\end{matrix}\right\}N, HO.$

On adding a watery solution of oxalic acid to this base

dissolved in spirits of wine, a white crystalline precipitate is formed. This was separated by filtration, and recrystallized from boiling water. The crystals formed on cooling were indistinct in form, and with difficulty soluble in alcohol and water; insoluble in æther. The combustion of a portion dried at the ordinary temperature gave the following results:—

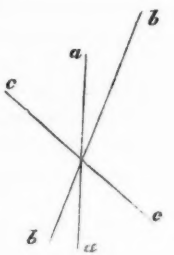
0·5635 grm. of the oxalate gave 0·8045 grm. of carbonic acid and 0·1695 grm. of water. These numbers correspond to the formula $C_2 O_3, C_{12} \left\{ \begin{matrix} H_6 \\ Br \end{matrix} \right\} N + HO$, as is seen by a comparison of the theoretical and experimental numbers.

			Theory.		Experiment.
14 equiv.	Carbon .	=	1050·0	38·99	38·93
7 ...	Hydrogen	=	87·50	3·24	3·34
1 ...	Bromine .	=	978·31		
1 ...	Nitrogen .	=	177·04		
4 ...	Oxygen .	=	400·00		
1 ...	Oxalate of Bromaniline	=	2692·85		

So that the brominated base forms, like aniline, the neutral oxalate under the same circumstances in which the acid salt of chloraniline is obtained.

Hydrochlorate of Bromaniline. $Cl\,H, C_{12} \left\{ \begin{matrix} H_6 \\ Br \end{matrix} \right\} N.$

This salt, which is obtained directly by dissolving bromaniline in hydrochloric acid, crystallizes on cooling from its hot saturated solution in a radiating filamentous mass. By slow evaporation of the solution over sulphuric acid, large well-formed crystals can be procured.



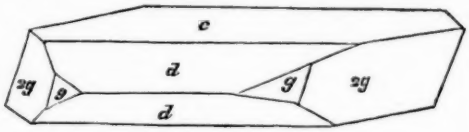
According to the determination of Dr. T. Müller, these crystals belong to the monoclinometric system (system hemiorthotype of Mohs).

The angle which is formed by the horizontal axis b and a is $=90°$. The axis c forms with a a right, and with b an oblique angle.

Names of the planes:—

$$c = c : \infty a : \infty b$$
$$d = a : c : \infty b$$
$$g = a : b : \infty c$$
$$2g = 2a : b : \infty c$$

The oblique rhombic prism $2\,g$ is terminated by the end planes c in such a manner, that the crystals present a tabular appearance. The acute edges of the prism are truncated by



the planes d and g. The planes g do not present themselves at all, or if so, it is in the form of small triangles.

From the measurement of the angles result the following relation between the axes:—$b : a : c = 1 : 0{\cdot}989 : 0{\cdot}843$, and the angle between the axes c and $b = 72^\circ\ 20'$.

This salt is isomorphous with the hydrochlorate of chloraniline. It belongs to the same crystalline system, and is formed by the same planes. Still the character is somewhat different, viz. the crystals are less extended in the direction of the axis b, so that the horizontal edge, in which the two planes a cut each other, disappear, and the two planes d with the two g form a four-sided summit: the angle of the prism $2\,g : 2\,g$ was found here $= 127^\circ\ 48'$. The angles of this salt however can not be so well measured as in the analogous one.

The analysis of the hydrochlorate of bromaniline gave the following results:—

1·1425 grm. of the salt gave 0·798 grm. of chloride of silver.

This corresponds to the formula $\mathrm{Cl\,H,\ C_{12}}\left\{\begin{matrix}\mathrm{H_6}\\ \mathrm{Br}\end{matrix}\right\}\mathrm{N}$, as is shown by the following calculation:—

		Theory.		Experiment.
1 equiv.	Base	= 2130·35	82·40	
1 ...	Hydrochloric acid	= 455·15	17·60	17·71
1 ...	Hydrochlorate of Bromaniline	= 2585·50	100·	

Bromaniline and Bichloride of Platinum,

$$\mathrm{Cl\,H,\ C_{12}}\left\{\begin{matrix}\mathrm{H_6}\\ \mathrm{Br}\end{matrix}\right\}\mathrm{N} + \mathrm{Cl_2\,Pt},$$

is precipitated by mixing hydrochlorate of bromaniline with bichloride of platinum, and cannot be distinguished either in its relations or aspect from the platinum salt of the corresponding chlorine base. The analysis already given by the determination of the atomic weight furnished 26·19 per

cent. platinum, from which is deduced the formula Cl H, $C_{12}\left\{\begin{matrix}H_6\\Br\end{matrix}\right\}N + Cl_2 Pt$, which requires 26·22 per cent.

ACTION OF FUSED HYDRATE OF POTASH ON DIBROMISATINE (*Bibromisatine*, Erdmann, *Bromisatinese*, Laurent).

F. *Dibromaniline* (*Amabrophenese*). $C_{12}\left\{\begin{matrix}H_5\\Br_2\end{matrix}\right\}N$.*

By the distillation of dibromisatine with hydrate of potash there passes into the receiver likewise an oily body, which solidifies into a crystalline mass. By washing these crystals with water till all trace of ammonia, which is formed in the last stage of the distillation, is removed, and dissolving in boiling alcohol, they are obtained of a shining white appearance.

a. Composition of Dibromaniline.

A very sure conclusion on the composition of this body may be drawn from analogy. I therefore contented myself with a determination of the carbon and hydrogen.

On burning with chromate of lead the following results were obtained:—

0·2795 grm. of the substance gave 0·2950 grm. of carbonic acid and 0·065 grm. of water. These numbers correspond in the 100 parts to

Carbon	28·77
Hydrogen . . .	2·40

Corresponding formula, $C_{12}\left\{\begin{matrix}H_5\\Br_2\end{matrix}\right\}N$, as is shown by the following:—

			Theory.		Experiment.
12 equiv.	Carbon . .	=	900·00	29·06	28·77
5 ...	Hydrogen .	=	62·50	2·01	2·40
2 ...	Bromine . .	=	1956·62		
1 ...	Nitrogen . .	=	177·05		
1 ...	Dibromaniline	=	3096·17.		

* The dibromisatine employed was prepared by long digestion of bromisatine with bromine. The substance crystallized from alcohol and burned with chromate of lead gave the following results:—

0·406 grm. of substance gave 0·4715 grm. of carbonic acid and 0·047 grm. of water. These numbers correspond in the 100 parts to

Carbon	31·62
Hydrogen	1·28

and indicate the formula $C_{16}\left\{\begin{matrix}H_3\\Br_2\end{matrix}\right\}NO_4$, which requires

Carbon	31·83
Hydrogen	1·00

b. Properties of Dibromaniline.

These I have not as yet very carefully studied. They resemble in many respects those of bromaniline. The crystals of this body, however, have a totally different form. It does not crystallize in octahedrons as the bromaniline, but in flat, four-sided, rhombic prisms of considerable size, which unfortunately present no terminal planes.

The base is soluble in spirits of wine and yields successive crops of crystals to the last drop. It is only slightly soluble in boiling water, which becomes turbid on cooling, and deposits gradually fine white needles. The crystals of the base melt, between 50° and 60° cent., to a dark oily fluid, which frequently on cooling remain long liquid, but on agitation suddenly solidify to a crystalline mass.

A solution of the base in acids communicates, like aniline, a yellow colour to fir-wood and the pith of the elder tree.

The compounds of dibromaniline have likewise as yet not been the object of particular study. I will only mention a few observations which appeared to me essential to the establishment of the chemical characters of dibromaniline.

It possesses the properties of a base; its basic character is however much less pronounced than that of bromaniline. It dissolves in acids, and is again precipitated by alkalies. Its solution in hydrochloric acid gives with perchloride of iron the crystalline orange-yellow precipitate, characteristic of organic bases. It forms with acids crystalline salts, but these compounds possess much less stability than the corresponding salts of bromaniline.

A solution of the base in boiling hydrochloric acid deposits on cooling a salt which crystallizes in plates.

0·2313 grm. of these crystals, precipitated with nitrate of silver, gave 0·1205 grm. of chloride of silver, corresponding to 13·21 per cent. of hydrochloric acid. This determination leads to the formula Cl H, $C_{12}\left\{\begin{matrix}H^5\\Br_2\end{matrix}\right\}N$, as is seen by the following:—

		Theory.		Experiment.
1 equiv.	Base . . .	= 3096·17	87·19	
1 ...	Cl H . . .	= 435·15	12·81	13·21
1 ...	Hydrochlorate of dibromaniline	= 3551·32	100·00	

This substance is decomposed by the action of warm water. The base separates from the acid and swims on the surface of the fluid in the form of oily drops. This want of stability in the hydrochloric compound is also seen when the base is dis-

solved in a great excess of acid and placed under a bell-glass with caustic lime. After some time crystals are obtained, which are only slightly soluble in water, and consist almost entirely of pure base. The elasticity of the hydrochloric acid is thus sufficient to overcome the affinity between it and the base.

G. *Tribromaniline* (*Amabrophenose*). $C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N$.

This compound has been long since described by Fritzsche* and named by him bromaniloid. He obtained it by treating aniline with bromine. It forms with the same facility by the action of the same body on bromaniline or dibromaniline.

I have prepared this body from bromaniline. The hydrochlorate of this base gives with a solution of bromine in water a white precipitate with a tint of violet. As the violet colour did not disappear by re-crystallization from alcohol, I submitted the compound to distillation. At the commencement of the distillation there are condensed in the receiver beautiful snow-white crystals; towards the end however the violet accessory product also passed over, and could not be removed again by recrystallization from alcohol. Although the properties and mode of formation of this body left no doubt of its identity with bromaniloid, I however made a combustion of it. Unfortunately, as stated, the substance was not perfectly pure, hence the proportion of carbon is too high.

0·3305 grm. of substance gave 0·2800 grm. of carbonic acid and 0·0450 grm. of water; corresponding in the 100 parts to

Carbon	23·10
Hydrogen . . .	1·51

The formula will therefore be $C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N$, which requires

Carbon	22·15
Hydrogen . . .	1·22

Tribromaniline is not a base but an indifferent substance, and does not combine with bases or acids. I must refer to Fritzsche's memoir for the description of its properties.

The following table exhibits the formulæ of the different bodies which form the subject of this paper:—

Aniline . . . }
Amaphenase . . } $= C_{12}H_7N$

Substitution of the hydrogen by chlorine.

Chloraniline . . }
Amachlophenese . } $= C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N$

* *Bullet. Scient. de St. Pétersb.*, 1843, t. i. p. 30.

$$\left.\begin{matrix}\text{Dichloraniline} \\ \text{Amachlophenise}\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_5 \\ Cl_2\end{matrix}\right\}N$$

$$\left.\begin{matrix}\text{Trichloraniline} \\ \text{Amachlophenose}\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_4 \\ Cl_3\end{matrix}\right\}N$$

Substitution of the hydrogen by chlorine and bromine.

$$\left.\begin{matrix}\text{Chlorodibromaniline} \\ \text{Amachlobrophenose}\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_4 \\ Cl \\ Br_2\end{matrix}\right\}N$$

Substitution of the hydrogen by bromine.

$$\left.\begin{matrix}\text{Bromaniline} \\ \text{Amabrophenese}\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_6 \\ Br\end{matrix}\right\}N$$

$$\left.\begin{matrix}\text{Dibromaniline} \\ \text{Amabrophenise}\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H^5 \\ Br_2\end{matrix}\right\}N$$

$$\left.\begin{matrix}\text{Tribromaniline} \\ \text{Amabrophenose}\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_4 \\ Br_3\end{matrix}\right\}N.$$

We now return to the question, can chlorine play the part of hydrogen in organic compounds?

The isatine group is perhaps quite capable of affording some explanation of this question.

In isatine we have a body which, by the action of chlorine, loses one or more equivalents of hydrogen, which are replaced by the acting substance. These three compounds, isatine, chlorisatine and dichlorisatine, possess the same chemical and physical properties. By the substitution of chlorine for hydrogen the character of isatine has not been changed. Isatine, chlorisatine and dichlorisatine, by the action of other agents, suffered similar changes. By treatment with sulphuret of ammonium we see these three bodies assuming one equivalent of hydrogen and changing into isatyd, chlorisatyd and dichlorisatyd. By proper treatment with sulphuretted hydrogen the whole or part of the oxygen can be eliminated and replaced by sulphur. In contact with alkaline sulphates the sulphoisatinic and chlorisatinic salts are formed; peculiar compounds, in which the sulphurous acid is united in a singular manner with the organic substance. The behaviour of isatine and chlorisatine to ammonia and alkalies is also similar: particularly towards the latter the analogy in their action is in the highest degree characteristic. At the ordinary temperature they unite directly with the alkalies, but at a boiling heat they change into isatinic and chlorisatinic acid, whose strict analogy in all these salts never fails. Finally, by fusion with hydrate of potash, we see isatine converted into aniline; when chlorisatine is treated in the same manner, still under conditions which certainly are favourable to fix the chlorine, this

element is observed to pass over into the new compound. From the fused hydrate of potash, which retains a portion of the carbon of chlorisatine in the form of carbonic acid, there distils over chloraniline, and with it the whole of the chlorine existing in the former compound. In the present memoir I have had frequent occasion to show the analogy which exists between aniline and the chlorinated base; it extends not only to the fundamental properties of both bodies, but even to the products of decomposition. By the action of bromine on aniline tribromaniline is formed, $C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N$; with the chlorinated base the same body gives chlorodibromaniline, $C_{12}\left\{\begin{matrix}H_4\\Cl\\Br\end{matrix}\right\}N$, which in no respect, either in its properties or characters, can be distinguished from the preceding. The only difference of the two compounds consists in the presence of chlorine in the second body.

On the preceding facts, when considered together, it appears to me that no two constructions can be entertained. They prove, in an undoubted manner, that in certain circumstances chlorine or bromine can perform the part of hydrogen in organic compounds.

It is quite another question, Is every organic body capable of assuming chlorine in the place of its hydrogen?

Further, in those organic compounds in which we see one or two equivalents of hydrogen replaced by chlorine, without any essential modification of their fundamental characters, is it possible to make a complete substitution of these elements without changing the properties of the compounds?

For the definite solution of these questions many further investigations must still be made. From the foregoing experiments it appears, however, that the chlorine preserves, to a certain extent, its electro-negative character in those compounds in which it replaces hydrogen, and that in proportion to the increase in the number of equivalents of the latter for which chlorine or bromine are substituted, so is this character the more impressed on the resulting compounds. The compound atom aniline, $C_{12}\,H_7\,N$, in consequence of the peculiar arrangement of its elements, possesses the property of uniting with an acid; replace one equivalent of its hydrogen by bromine, and we obtain bromaniline; a body possessing likewise basic properties, but in a feebler degree. A number of metallic oxides, which can be precipitated from their solutions by aniline, are not affected by the brominated base. Bromaniline is a less powerful base than aniline. By the assumption

of the equivalent of the electro-negative body bromine, the basic properties of the original system is enfeebled; substitute now another equivalent of bromine for hydrogen, and we have dibromaniline. The facility with which, as we mentioned, all its salts are decomposed, evidently indicates that the basic character of aniline is further enfeebled by the repeated assumption of bromine. Finally, in tribromaniline the electro-negative properties of the assumed bromine equivalents have placed themselves in equilibrium with the electro-positive character of the original system. Possibly, by the further addition of bromine, a body may be formed possessing acid properties.

We have in inorganic chemistry the compounds of many metals with oxygen which exhibit in a distant degree the same character; for distant I must call it, since it is not a question of substitution. Protoxide of manganese is a strong base, whilst in the sesquioxide, richer in oxygen, the basic properties are lessened; peroxide of manganese unites with neither base nor acid, and by the addition of more oxygen we have manganic and hypermanganic acid generated.

It is only with the greatest diffidence I venture to express an opinion on this subject: nothing is more dangerous than to wish to draw general conclusions without having a mass of facts at command.

Bromaniline and dibromaniline possess, though in a lesser degree, the fundamental properties of aniline—they are bases. Tribromaniline is neutral; in it the original character of aniline has entirely disappeared. This body was however produced in a totally different way from that of the two brominated bases. It may be objected, that in it the grouping of the atoms, as they prevailed in the original system of aniline, no longer remained. Possibly there may exist a body of the same composition having the formula $C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N$, which still possesses basic properties. Such a body would be formed by distilling tribromisatine, $C_{16}\left\{\begin{matrix}H_2\\Br_3\end{matrix}\right\}NO_4$, with hydrate of potash. This compound is as yet unknown. Further experiments must therefore be made to solve the question.

Before concluding this memoir I shall mention another compound which appears worthy of the attention of chemists.

It is formed by passing into aniline free from water a stream of cyanic acid obtained by distilling cyanuric acid. The fluid becomes considerably heated, and solidifies on cooling into a crystalline mass. These crystals are insoluble in water, but soluble in boiling alcohol, from which they are deposited in

white shining plates. It contains neither cyanic acid nor aniline. It may be heated with hydrochloric acid or potash without decomposition. It is a kind of urea, in which the ammonia is replaced by aniline. I was in hopes that this body would possess basic properties, and like urea form crystalline salts with nitric and oxalic acid; its properties are however totally different.

I shall in a separate memoir return more fully to this product of the decomposition of aniline.

February 17, 1845.—The President in the Chair.

Mr. Cock presented two Specimens of finely laminated Palladium to the Society's Museum.

Dr. R. D. Thomson presented a printed memoir "On the Production of Soils and Manures by the lower order of Plants."

In accordance with the laws of the Society, the Council announced the names of the Vice-President and Members of Council whom they recommended should retire, namely, Thomas Graham, Esq., Vice-President; Thomas Everett, Esq., M. Faraday, D.C.L., Percival N. Johnson, Esq., and William H. Miller, Esq., M.A.; and declared the names of the following gentlemen to supply their places: A. Aikin, Vice-President; Robert Kane, M.D., John Cock, Esq., James Lowe Wheeler, Esq., and Warren De la Rue, Esq.

The names of the Officers recommended by the Council for election were also declared:—President, Thomas Graham, Esq.; Vice-Presidents, A. Aikin, Esq., W. Thomas Brande, Esq., J. T Cooper, Esq., and Thomas Thomson, M.D.; Treasurer, Robert Porrett, Esq.; Secretaries, Robert Warington, Esq., and George Fownes, Ph.D.; Foreign Secretary, E. F. Teschemacher, Esq.

The following communications were then read:—

CXXX. *On the Structure of Electro-precipitated Metals.* *By* Warren De la Rue, *Esq.*

THE following observations, being the result of an extensive series of experiments on the practical application of the processes of electro-metallurgy, will, I am induced to believe, be acceptable to the Chemical Society.

The various appearances of the metallic deposit are familiar to all manipulators in electro-metallurgy, and are distinguished by the names crystalline, lesser crystalline, malleable, sandy and spongy; the latter being produced by an excess of power in the battery, the first by too small a power in relation to the strength of the solution operated on. All these deposits are however merely modifications of each other, they are essentially crystalline, and even the malleable, or in other

words the most cohesive, is very inferior in strength to metals wrought by the processes in ordinary use.

The malleable is that deposit usually required; yet, even with all the art of a practised electro metallurgist, it is difficult for a lengthened period to obtain it, inasmuch as the power of the battery, the temperature of the air, and consequently the conducting power of the fluids composing the circuit are constantly changing their relation to the strength of the electrolyte to be decomposed. There are other causes presently to be considered which also play an important part in producing these difficulties, and which we shall better understand by considering what effect the form of the matrix and the nature of its original surface have on the resulting precipitate.

It is well known to persons conversant with the precipitation of metals from their respective solutions by means of voltaic electricity, that these solutions become exhausted of the metal at the cathode to such an extent, that if we place the cathode on the surface of the liquid all action after a short time ceases: the exhausted liquid being specifically lighter, no mechanical transfer of fresh liquid takes place*, and consequently the process is stopped. This exhaustion of the electrolyte is the primary cause of the difficulties of the process.

If, for example, an attempt be made to produce a solid medal by depositing between the respective matrixes of the obverse and reverse, the attempt would undoubtedly fail; the opposite and approaching deposits never join and form one solid piece. The cause of this is sufficiently obvious, and can be easily traced to the exhaustion of the electrolyte; for as the opposite deposits approach they render the cavity smaller and smaller, and at last it becomes so reduced that its capillarity interferes with the renewal of the liquid, and eventually the action ceases, a cavity containing the exhausted liquid remains, and no true juncture takes place.

The following experiment proves, in a striking manner, that the preceding is not merely a conjectural case. I prepared a matrix by cutting angular lines about one-twentieth of an inch deep in a metallic plate, the angle of the opening being about 35 degrees. On this was deposited copper to about the eighth of an inch in thickness; the deposit was what would be termed exceedingly good, and, to a practised eye, uniform, there being but a slight indication of the original lines at the back of

* Professor Daniell and Dr. Miller, in a paper on the electrolysis of secondary compounds, have entered into the investigation of these phænomena.

the cast; yet the copper could be broken with great facility through the centre of each line, in a plane bisecting the angle, presenting to the eye a very smooth and uniform fracture, and giving the idea of its having been rather purposely cut through than broken at random. Here we have an example of the interstitial space being not only left between the walls of the original groove, but existing through the additional eighth of an inch of deposited metal, from the obvious cause of the incapability of the included liquid acting the part of a cathode. Plate I. fig. 1 is a diagram of the section through the matrix and deposited copper; A being the matrix, B the deposited metal.

A matrix from a wood engraving presents a good example of the effect which the form of the mould has on the resulting deposited counterpart: in it we have a vast assemblage of minute grooves, the reverse of the lines in the engraving; these grooves are never perfectly filled, from the cause before stated, and the deposit is consequently cut up into an assemblage of minute pieces, joined *apparently though not in reality*, and nicely held together by the intricacy of their interlacings. The sky, from its consisting of a number of straight lines in the engraving, is especially tender and troublesome to obtain perfect. Though I have chosen the copy of a wood engraving as an example, from its presenting an extreme case of difficulty, yet the same effect is produced under other circumstances; for instance, in the silver coating of a cylindrical vessel having a flat bottom; in it there will infallibly exist a fissure at the angle formed by the cylinder and the bottom. Hence we see the necessity of *rounding off* as much as possible all angles where we intend to deposit metals with the aid of electricity.

The surface of the mould must consequently have an obvious effect on the deposit, inasmuch as no surface can be perfect in its polish; hence it must necessarily follow that the more gradual the undulations and depressions are, the more cohesive will be the deposit; a wax matrix is perhaps one of the best substances to deposit on, and a polytype matrix, obtained by pressing a woodcut into a melted metallic alloy when near its point of solidification, one of the worst, for we have on it a copy of all the pores of the wood; besides, the alloy being crystalline, its surface is, when microscopically examined, exceedingly rough. All abrupt deviations from the original plane, though small, have an injurious effect on the resulting deposit, and this increases with the depth; but deep or shallow, the result is the same, and differs only in amount.

I have stated that all electro-metallic deposits are essentially crystalline in their structure; this is readily proved by submitting them to the test of microscopic investigation, and however carefully they be prepared, we shall perceive that they consist of an assemblage of minute crystals more or less perfectly formed. In fig. 5 is represented a portion of a beautiful deposit on a polished piece of metal after five minutes' action, the magnifying power employed being 300 times. In it the crystalline structure is rendered apparent, and we see moreover, here and there, groups of crystals starting up perpendicularly from the surface to a considerable height. Such being the character of the first layers, the crystals, as in the crystallization of a salt from its solution, increase in size, and could we even obtain a perfect surface to commence on, we must have, from the very nature of the process, the production of inequalities, to which the shooting of these crystals above the general surface mainly contributes; these irregularities, as before explained, can never perfectly be filled up, and a porous structure must result; add to this, that the crystallization likewise spreads laterally from the summit of one group of crystals to that of those in the neighbourhood, and it will be readily perceived that spaces are here and there enclosed, which can only become filled to the extent that the included liquid is capable of yielding metal. Hence the microscope reveals a structure such as I have delineated in fig. 2, which is a section of electro-deposited copper magnified 100 times linear; the section is a cutting made with sharp scissors through a plate of about the fortieth of an inch in thickness, having the character of the lesser crystalline, and appeared to the unassisted eye perfectly polished and compact. Fig. 3 is a representation of the back of the same specimen, showing clearly its crystalline structure; this is likewise magnified 100 times. Even the most compact specimens present, under a sufficient magnifying power (see fig. 5), the same porous appearance; the pores are smaller, it is true, but greater in number, and the character of the deposit is the same. I here again repeat that the electro-metallic deposit is essentially crystalline in structure; in fact it is but a tissue of crystals *interlacing* but *not adhering*. We may diminish the power of the battery with respect to the quantity of metallic salt present in the electrolyte, so as to obtain, by these favourable circumstances, large and well-formed crystals,—we may go on increasing the power, and produce the crystals more and more hurriedly, and consequently smaller and smaller and less perfectly formed, but we ultimately reach a point in the quantity

of electricity transmitted, that, if we increase it, the electrolyte cannot be renewed with sufficient rapidity at the surface of the cathode, and we have larger spaces left unfilled, thus producing the sandy deposit. Lastly, we may increase it to so great an extent that the metal assumes the form of the spongy deposit; but still all are crystalline.

The ridges or lines which are frequently seen at the back of electro-casts, placed vertically in the trough, more especially in those where there are sharp angles jutting out from the matrix, are produced by these points impeding the upward flow of partially exhausted liquid, and causing it to run in little detached streams; where these exist *there* the deposit is formed less quickly than in those parts where the liquid is stronger, consequently we have a hollow or groove produced, which remains permanent. To produce an interchange of the fluid in the precipitating troughs, a constant stream of fresh liquid was caused to run in at the bottom whilst the weak fluid overflowed at the top: the resulting current in meeting the upward flow of the fluid at the surface of the electro-cast produced a series of vortices, and changed the vertical ridges into a series of curiously-curved lines, which were equally objectionable; hence this scheme had to be rejected.

Fig. 4 is a magnified representation of a curious electro-deposit of silver, kindly furnished me by Mr. Napier, who has named it "silver sponge," from its resemblance to that substance. Under the microscope it is a most splendid arborescent assemblage of crystals, and presents us with an extreme case of crystallization in electro-metallic deposits. The drawing is made 200 times the natural size.

To return to an electro-copy of a wood engraving: it is found by examination under the microscope, and would be anticipated from the preceding remarks, that each line has a space in its centre; they are in fact exceedingly hollow, and present much the appearance of the hollow crystallized cakes of sugar made by confectioners, and hence we see the advantage of thoroughly tinning it at the back as soon as we have removed the cast from its matrix; the tin insinuates itself into a great number of the pores and binds the whole firmly together. With the help of a little chloride of zinc the tinning is effected very readily, and should be done without disturbing the structure by filing.

There is one phænomenon, connected with the employment of electro-casts, exceedingly curious—it is their uselessness for printing with vermilion ink (sulphuret of mercury), which is not the case with respect to ordinary engraved copper

blocks. When an electro-cast is inked over with vermilion printing ink, and a few impressions have been taken, the vermilion is blackened, and as the process is continued the copper begins to get white, and at last so much mercury is precipitated on the surface as to prevent the adherence of the ink. I am inclined to think that the porous and divided nature of the electro-cast is the sole cause of its decomposing the vermilion, and that the purity of the copper is not concerned in it.

In most of the preceding remarks I have alluded to deposits of copper, but I wish it to be understood that they apply equally to gold, silver or other metals; and such being the nature of precipitated metals, I consider that though the electro-metallurgic processes are a valuable addition to the arts, there are uses to which they should not be applied; as, for example, the coating of one metal with another when it is intended to protect the covered metal from the action of certain fluids, at all events without the precaution in all possible cases of subsequently partially fusing the coating metal.

The production of ornamental pieces of plate, and the silvering or gilding of such objects as are not subject to much friction, is not open to the same objections. Platinum and palladium also, if ever obtained by the electro-metallurgic process in plates or other forms, should subsequently be subjected to the process of welding and hammering. It has been proposed to copper the bottoms of ships by this process; apart from the great difficulty of effecting this on a large scale, the copper in my opinion would be far too friable for such a use. Copper duplicates of steel or copper engravings, it is well known, are not nearly so durable as the original plates, yet in some cases they may be advantageously employed,—not however where very large numbers are likely to be required, as, for example, in the printing of bank notes. I was once consulted as to the practicability of coating the interior of the air-pumps and the valve facings of large marine engines by the electro-metallurgic process, and I include this as one of the improper applications of the art. In conclusion, I again repeat, that the processes of electro-metallurgy are a valuable acquisition to the arts, yet it is necessary to bear in mind its defects, in order that we may not apply it to purposes for which it is unfitted.

CXXXI. *On the true Composition of Chlorindatmit.* By August Wilhelm Hofmann, *Ph.D.*

IN a preceding memoir on the Metamorphoses of Indigo, I have described under the name of trichloraniline a body which may be regarded as aniline, in which three equivalents of hydrogen are replaced by an equal number of chlorine:

$$\text{Aniline} \quad . \quad . \quad . \quad = C_{12} H_7 N$$

$$\text{Trichloraniline} \; . \quad = C_{12} \left\{ \begin{matrix} H_4 \\ Cl_3 \end{matrix} \right\} N.$$

I had already, a year and a half ago, observed the formation of this body by the action of chlorine on aniline*, but at that time the quantity obtained was so small that I was obliged to content myself with a conjectural opinion of its constitution. More lately I found that the same substance was produced by the treatment of chloraniline with chlorine. Even by the last-mentioned way the quantity obtained was but small. With all my efforts I could not obtain more than was just sufficient for one combustion, which unfortunately gave somewhat too much carbon†. Although myself thoroughly convinced of the exactness of the given formula,—the method of formation of this body, the complete analogy with tribromaniline and chlorodibromaniline, independently of the analysis adduced, being sufficient evidences,—I thought it however desirable to place the composition of trichloraniline beyond every doubt by the production of better numbers.

At first I thought of obtaining these numbers by a repetition of the preparation and analysis, until I found the object could be attained by a much more convenient way.

For this purpose I must here mention some results obtained by Erdmann in his excellent investigation on indigo.

If indigo suspended in water be treated with chlorine, it is transformed, as is known, into a reddish yellow mass, which is a mixture of different substances. On submitting this to distillation with water, chlorisatine and dichlorisatine remain in the retort, whilst another body volatilizes with the watery vapour, which according to Erdmann contained no nitrogen. He called this substance chlorindopten‡, and gave for it the following formula:

$$C_{32} H_8 Cl_8 O_4.$$

By later experiments Erdmann found however that on distilling chlorindopten with potash or carbonate of potash it is

* Liebig's *Ann.* vol. xlvii. p. 68, and Phil. Mag.

† See the preceding Memoir.

‡ *Journ. für Prakt. Chem.*, Bd. xix. p. 334.

decomposed into a neutral body which passes over, and an acid which remains in the retort united to the potash. The latter is chlorindoptenic acid (chlorophenisic acid of Laurent); the former Erdmann called chlorindatmit, and gave it the formula $C_{12} H_4 Cl_3 O_2$.

Whence comes this body? In what relation does it stand to the other members of the indigo or phenyle series? Among the many derivatives of indigo made known to us by the investigations of Erdmann and Laurent it stands quite isolated.

On comparing the properties which Erdmann described as belonging to chlorindatmit with those I had observed in trichloraniline, it appeared to me in the highest degree probable that these bodies were identical. The properties of both bodies correspond exactly, and the method of formation is extremely alike. The production of trichloraniline, as well as that of chlorindatmit, is accompanied by the formation of chlorindoptenic acid. Erdmann had determined the carbon, hydrogen and chlorine in chlorindatmit. His numbers correspond completely with the composition of trichloraniline. For comparison I placed together the theoretical numbers of this body and the analytical results of Erdmann.

Chlorindatmit.		Trichloraniline.	
Carbon . .	= 36·42*	Carbon . .	= 36·66
Hydrogen .	= 2·23	Hydrogen .	= 2·03
Chlorine . .	= 53·58	Chlorine . .	= 54·09
Loss . . .	= 7·79	Nitrogen . .	= 7·22
	100·00		100·00

Erdmann did not look for nitrogen in chlorindatmit as he had found none in chlorindopten. Did chlorindopten consist of equal equivalents of chlorindoptenic acid and chlorindatmit, such a compound (assuming chlorindatmit to be an azotized body) would contain 3·61 per cent. nitrogen, a quantity which could not have been overlooked. It is, however, not composed of a like quantity of each element, but the chlorindoptenic acid predominates very much, so that the amount of nitrogen is much reduced, and may be easily overlooked. On the other hand, the proportion of carbon and hydrogen cannot essentially alter, as chlorindoptenic acid and chlorindatmit contain nearly equal quantities.

To determine this question by experiment, I treated with chlorine, according to Erdmann's method, a quarter of a pound of reduced and again oxidized indigo suspended in water. Although the operation was conducted in sunshine, yet it was only after three or four days that the indigo was

* The equivalent of carbon is here taken as 75.

converted into the brownish-yellow body. The whole mass, together with the fluid, was poured into a retort and distilled over an open fire. In the receiver a yellow crystalline substance condensed and swam on the surface of the water, which had also passed over and contained hydrochloric acid. The distilled product was saturated with potash ley, which communicates a dark colour to the fluid from the solution of a portion of the crystals, and the whole was again submitted to distillation. By gently warming the retort, a vapour was evolved which condensed in the neck in the form of fine white crystals like hairs, about an inch long, which, on bringing the fluid to the boiling-point, passed over with the watery vapours as an oil and again crystallized in the receiver. The crystals were separated by filtration and dried. The investigation was confined to the single question, whether chlorindatmit so prepared contained nitrogen or not?

On passing the vapour of chlorindatmit over fused potassium a large quantity of cyanide of potassium was formed, which evolved freely hydrocyanic acid on the addition of an acid. A mixture of a proto- and persalt of iron produced a gray-brown precipitate, which assumed the pure colour of Berlin blue by the addition of a little hydrochloric acid. Further, on heating with the soda-lime mixture a quantity of ammonia was given off. Chlorindatmit therefore contains nitrogen.

From the preceding facts several conclusions may be drawn.

1st. The body produced by the action of chlorine on aniline and chloraniline has in reality the following composition:

$$C_{12}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right\}N.$$

2nd. The chlorindatmit of Erdmann is nothing but trichloraniline.

3rd. The name chlorindopten merely denotes an indefinite mixture of chlorindoptenic acid and trichloraniline.

The formation of trichloraniline by the action of chlorine on indigo is not at all surprising. The transformation of indigo into nitropicric and chlorindoptenic acids, and into aniline, proves sufficiently that there are present in this body the conditions necessary for the production of all the members of the phenyle series. The action of potash and of chlorine on indigo is in this respect essentially the same. The only difference is, that in the first instance a pure product of oxidation is obtained, whilst in the second a number of the hydrogen equivalents of this product is replaced by a corresponding number of the oxidizing agent, viz. chlorine. In the one case aniline is formed, in the other trichloraniline. The latest in-

vestigations of Cahours*, in which he succeeded in obtaining salicylic acid by treating indigo with hydrate of potash, show that out of this latter substance hydrate of phenyle can likewise be produced, the compound free from chlorine, which corresponds to chlorindoptenic acid.

In an analogous manner Erdmann† obtained, by the action of bromine on indigo, bromisatine, dibromisatine and bromindopten. This last substance, distilled with potash, is decomposed into bromindoptenic acid and bromindatmit. Erdmann did not analyse bromindatmit; but it is scarcely necessary to remark that this body is nothing but tribromaniline (Fritzsche's bromaniloid),

$$C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N.$$

CXXXII. *Analyses of Farm-Yard Manure, and of Coal-Gas.* By Thomas Richardson, *Esq.*

THE accompanying analysis of farm-yard manure is part of an investigation in which I am at present engaged, and the results show, rather unexpectedly, that this manure has a somewhat similar composition in different localities. (See Boussingault's *Economie Rurale.*) The methods of analysis were those in general use. The manure was an average sample, and taken just previous to its being applied to the soil.

Farm-Yard Manure.

1. *Fresh.*

Water	64·96	
Organic matter	24·71	
Inorganic salts, &c.	10·33	100·00

2. *Dried at* 212°.

Carbon	37·40	
Hydrogen	5·27	
Oxygen	25·52	
Azote	1·76	
Ashes	30·05	100·00

3. *Inorganic Matter.*

A. *Portion Soluble in Water.*

Potash	3·22	
Soda	2·73	
Lime	0·34	
Magnesia	0·26	
Sulphuric acid	3·27	
Chlorine	3·15	
Silica	0·04	13·01

* *Compt. Rend.*

† *Journ. für Prakt. Chem.*, Bd. xix. p. 358.

B. *Portion partially Soluble in Muriatic Acid.*

Silica	27·01	
Phosphate of lime . .	7·11	
Phosphate of magnesia.	2·26	
Phosphate of iron . .	4·68	
Phosphate of manganese	trace	
Phosphate of alumina ?.	trace	
Carbonate of lime . .	9·34	
Carbonate of magnesia .	1·63	
Sand	30·99	
Carbon	·83	
Alkali and loss . . .	3·14	86·99
		100·00

The following analyses are of the coal-gas which is supplied to the town of Newcastle-on-Tyne. It contained in 100 parts,—

	I.	II.
Olefiant gas	10·19	9·25
Carburetted hydrogen.	31·35	36·05
Hydrogen	28·80	30·17
Carbonic oxide . .	16·28	11·42
Azote	13·35	14·01
Carbonic acid . . .	a trace	a trace
Atmospheric air . .	0·48	0·50
Naphtha vapour . .	a trace	a trace
Ammonia	a trace	——
	100·35	101·40

March 3, 1845.—Thomas Graham, Esq., Vice-President, in the Chair.

Mr. Wm. Richardson presented a specimen of lead which exhibited on its surface the beautiful colours arising from oxidation, the production of which he explained in a short note.

John Mitchell, Charles Cowper, and A. J. Bernays, Esquires, were elected Members; and Aug. W. Hofmann, Ph.D., a Foreign Member of the Society.

The following papers were read:—

CXXXIII. *On a New Phosphate of Magnesia.* *By* Wm. Gregory, *M.D.*

A LETTER from Dr. Gregory was read, communicating the discovery of a new and remarkable phosphate of magnesia, of which the formula is $2\,MgO + 3\,PO_5$. This substance is dense and granular, and as completely insoluble as the sulphate of barytes. It is formed on heating magnesia, or any phosphate of magnesia, with excess of glacial phosphoric acid; and its production is likely to offer a superior process to those generally followed for the separation and quantitative estimation of that earth.

CXXXIV. *Contributions to Actino-Chemistry.* By Robert Hunt, *Esq.*, *Secretary to the Royal Cornwall Polytechnic Society, &c.*

MANY of the changes produced upon photographic preparations, by the influence of the solar rays, are of a remarkable character, and few of them in the present state of our knowledge can be satisfactorily explained. In some instances it would appear that new properties are imparted to bodies by exposure to sunshine; in others, that radiation has the power of disturbing the known chemical forces, and apparently establishing a new order of affinities; whilst in all we are forced to recognise the operations of a principle, the nature of which is involved in the most perplexing uncertainty. In the hope of being enabled to follow out some of these phænomena, under circumstances more favourable for investigation than those which offer themselves in the ordinary method of pursuing photographic experiments with the chemical compounds spread upon paper, where we have organic matter interfering with the results, I have been led to examine with attention the changes which take place under more simple conditions. It must be evident that a subject so extensive as this new branch of inquiry, embracing all material elements and their combinations, will not readily admit of satisfactory generalization; in this paper, indeed, I am scarcely able to do more than record a few facts, under particular heads, without any attempt at systematic arrangement.

To prevent any misinterpretation of terms, or confusion of ideas, it will be necessary to make a few preliminary remarks. The researches of Sir John Herschel and others most distinctly prove that the Light, Heat and Chemical Power of the solar rays are three distinct classes of phænomena. It has indeed been suggested they may be *distinct principles*, and a considerable amount of experimental evidence has been brought forward in support of this position. Without entering into the argument in this place, I desire simply to impress strongly the necessity of considering the *three effects* of luminous agency and colour, of calorific action, and of what has been called photographic influence, as phænomena depending upon three *things* (whether these be independent principles, or only modifications of one great immaterial element, not being here considered), to which it is necessary to give distinctive appellations. Light and heat are terms about which, in their familiar acceptation, there can be no mistake; but it is to be regretted that some confused terms have had the sanction of some eminent experimentalists, leading, as it appears to me, to a sad complexity of ideas. An "*invisible*

chemical coloration" is the hypothesis of one philosopher and "*invisible light*" the epithet of another, introduced in memoirs of great interest, in which the changes produced by the dark chemical rays, as they have been called, are sought to be explained. In support of this view it has been suggested that rays of light may exist which do not produce any excitement of the optic nerves of man, and it has been assumed that these rays may still be sufficiently powerful to produce vision in the night-roving animals; howbeit, of this there is not the slightest proof, and all the phænomena of vision in the cat, owl, and the like, in comparative, not absolute darkness, may be physiologically explained. However, in this paper LIGHT will be used to distinguish those radiations which produce vision and colour, HEAT, those affecting any thermic phænomena; whilst those radiations on which certain chemical changes are supposed to depend will be distinguished by the epithet of ACTINIC.

At the Meeting of the British Association at York, it was proposed by Sir John Herschel that all those phænomena which exhibit change of condition under the influence of the solar rays should be distinguished, as forming a peculiar province of chemistry, by the term ACTINO-CHEMISTRY, and this was generally approved by the Chemical Section. ACTINISM it is proposed shall in future be used to express that principle or modification upon which these phænomena depend. ACTINICITY will distinguish this power in action, and ACTINIZED I shall use to signify any substance which has been exposed to *Actinic* influence. In the progress of the examination of these physico-chemical phænomena other epithets must of necessity be formed; for example, it will be convenient to speak of media which obstruct the passage of actinism, like the quadri-sulphuret of lime and the solution of the bichromate of potash, as ADIACTINIC, whilst media admitting the free permeation of this power, as colourless glass, or a solution of the ammoniate of copper, would be distinguished as DIACTINIC*. Any instrument used for measuring the amount of chemical disturbance effected by the solar rays, would be called, as was proposed by Sir John Herschel, an ACTINOGRAPH. With these preliminary observations I do not think any difficulty will arise from the terms made use of in this paper.

INFLUENCE OF THE SOLAR RAYS ON PRECIPITATION.

In 1832 Sir John Herschel communicated the remark-

* These terms are formed from those proposed by M. Melloni in his "New Nomenclature for the Science of Calorific Radiations," a slight liberty being taken with them for the sake of euphony.

able fact, that when a solution of platinum in nitro-muriatic acid, which has been neutralized by the addition of lime, and has been well cleared by filtration, is mixed with lime-water in the dark, no precipitation, or scarcely any, takes place, but when (being thoroughly cleared of any sediment) this mixture is exposed to sunshine it instantly becomes milky, and a white or yellowish-white precipitate speedily falls.

By exposing this mixture behind coloured media, Sir John Herschel found that the effect was due to the influence of the most refrangible rays. I have placed this mixture in small glass tubes, and so arranged them that they were individually exposed to a separate ray of the spectrum. After an exposure of one hour the following results were obtained, the precipitates having been carefully washed and dried in the tubes in which they were formed.

Most refrangible rays beyond the visible spectrum	0·07 gr.
Violet rays	1·05 ...
Indigo rays	0·60 ...
Blue rays	0·45 ...
Green rays	0·10 ...
Yellow and orange rays	
Red rays	0·05 ...

It is a fact worthy of especial notice, that this precipitation is so dependent upon the amount of sunshine, that precipitates obtained in the same time, being carefully weighed off, will show the relative amounts of actinic influence to which they have been exposed.

Manganate of Potash.—A solution of this body having been made in the dark, was placed in two glass vessels and set aside. After having been kept in darkness for two hours, the solutions remained as clear as at first. One of the vessels with its contents was then removed into the sunshine, when the solution immediately became cloudy, and was very speedily decomposed, the precipitate falling heavily. By experiments with the spectrum, I have since found that the precipitation is due almost entirely to the more refrangible rays. I have not been enabled to decide with that degree of accuracy I could desire, in which ray the maximum effect is produced. The precipitates formed in the blue, indigo and violet rays were nearly of the same weight, but it did appear that the precipitation was most *speedily* produced by the mean *blue* ray.

If we dissolve the brown precipitate from the mineral chameleon in a solution of cyanide of potassium, we have a clear fluid. Reserve one portion in darkness, and expose another to good sunshine, the solution preserved in the dark will re-

main quite clear for many days, whereas that exposed to actinic influence throws down a brown precipitate after a few hours' exposure. If the solution is washed over paper, we procure by exposure good negative images of leaves or any other body superposed.

A few grains of sulphate of the protoxide of iron were dissolved in rain water. If kept in perfect darkness, the solution remains clear for a long time; it becomes, however, eventually cloudy and coloured from the formation of some peroxide of iron, even in tubes hermetically sealed. A few minutes' exposure to sunshine is sufficient to produce this change, and the oxide formed, instead of floating in the fluid, and as in the former case rendering it opake, falls speedily to the bottom.

Some years since, at the Meeting of the British Association at Plymouth, I published an account of an exceedingly sensitive "photographic" process, the agents employed being iodide of silver and the ferro-cyanide of potassium. I have since then made some experiments with the hope of ascertaining the rationale of the chemical changes which take place. This has not been done in anything like a satisfactory manner; they have, however, led me to observe a curious effect produced in mixed solutions of iodide of potassium and ferrocyanide of potassium under the influence of sunshine. If a mixture of these salts is kept in the dark, no change takes place for a long period, but if exposed to sunshine, the colour of the solution is much deepened, becoming of a bright golden yellow, and a light brown powder is precipitated. I have reserved the examination of this powder for some future period: I believe it to be a combination of iron and iodine, and I have good reason for believing that a very remarkable change takes place in the arrangement of the elements of the salts employed.

100 grains of the protosulphate of iron were dissolved in 2 oz. of distilled water; 30 grs. of the bichromate of potash were dissolved in 4 oz. of distilled water; 1 oz. of the iron solution was weighed into two large test-tubes, and 6 drachms of the solution of the bichromate of potash added to each, which formed a fine red-brown clear solution. One tube was kept from all light, and the other exposed to good sunshine for an hour; in both tubes there was a precipitation of the chromate of iron, described by Dr. Thomson in his memoir on the Salts of Chromium, published in the Philosophical Transactions. The solutions, which were perfectly clear, were poured off from the precipitates; these were washed and weighed. The precipitate formed in the dark was found to

weigh three grains more than that formed in the sunshine. This result was different from what my previous experiments had led me to expect, and it was several times repeated with the most scrupulous care. In every instance the precipitation which took place during *the first exposure* to sunshine was less than that formed in darkness.

The clear actinized solution poured off from the chromate of iron, being again exposed to solar influence, the other being carefully guarded from the slightest radiation, it was found that the precipitation went on much quicker in sunshine than in the dark; the side of the tube facing the sun was always thickly coated with chromate of iron, whilst the other side of it was perfectly free from any precipitation. Dr. Thomson has shown that this precipitation is produced by heat; it became interesting to know what part solar heat had in the phænomena. As I experienced some difficulty in arranging in a satisfactory manner many tubes along the prismatic spectrum, I used only three. One was placed in the mean indigo ray, another in the mean yellow ray, and the third in the least refrangible red ray. After an exposure of four hours, the precipitation formed in the tubes in the different rays were as follows:—

Indigo ray	5·25
Yellow ray	0·50
Red ray	2·15

Similar results were obtained by placing the solutions behind blue, yellow and red glasses, proving that although the calorific rays were not without action, the principal effect was due to the chemical rays. The half grain formed in the yellow ray I still regard as due to the thermic or actinic power of the beam, as behind a deep-coloured yellow solution (sulphate of potash and chromium) no precipitate was formed in eight hours.

I have made one or two other experiments (particularly one with a mixture of the bichromate of potash and the sulphate of copper) in which precipitation appears retarded by solar agency. I am rather inclined to think that it will eventually be proved that the electric energy of the different bodies in relation to each other will greatly modify the results we shall obtain in these experiments, and I intend, if possible, to investigate this part of the subject with care. Since Becquerel has shown (*Annales de Chimie*, November 1843) that the electrical excitation produced by the solar rays is different for each ray, and that this power is at its maximum in the yellow ray and also in the violet ray, the minimum force being between the green and blue rays; and since the mean maximum

of chemical energy has been shown to manifest itself in the violet ray, and its minimum invariably to reside in the yellow ray; and as it is known that the negative and positive currents or sparks produce opposite effects, may we not reasonably conclude that the solar radiations are in some remarkable manner involved in the production of electrical phænomena? To say, as has been said, that electricity is the agent producing the effects I have been considering, is rushing much too hastily to a conclusion; indeed, cases will be found in which, at the maximum of electrical power in the spectrum, electrical phænomena which would occur in darkness or in light, apart from heat or actinism, are entirely prevented.

Colour of Precipitates.

If a solution of bichromate of potash is exposed to sunshine, it acquires a property of precipitating several metals as chromates, differing many shades in colour from the colours produced by a similar solution prepared and kept in the dark. If the actinized solution be poured into a solution of nitrate of silver, the chromate of silver formed is of a much more beautiful colour than that given by a solution which has not been exposed to the sun. A like effect will take place in precipitating chromate of mercury with actinized and non-actinized solutions of the chrome salt.

Solutions of sulphate of iron exposed to sunshine yield a prussian blue with the ferro-prussiate of potash, of a far more beautiful colour than that produced by a solution which has not been so exposed. If solutions of both the salts are kept for many hours in good sunshine, the colour of the resulting prussian blue is still improved.

I have long noticed in the process of darkening photographic papers and Daguerreotype plates, that the colours produced varied in richness of tint and in shade with the brightness of the sun and the clearness of the atmosphere at the time of exposure. In some positive processes, in which a darkened paper was bleached under the influence of actinic radiations (if this expression be permitted), the effects of colour were often very striking and beautiful, whereas in winter, or when a slight haze existed, a dull dun-brown almost invariably resulted. It appears that dyers and the manufacturers of some of the fine pigments are not unacquainted with these facts; they are certainly curious, and deserve attentive investigation at the present time. I regret that I am only in a position to record the facts I have noticed, not having as yet determined even the influence of the various independent rays upon these coloured precipitations.

Actinic Influence on Chemical Combination.

Two phials were filled with a solution of acetate of silver and carefully corked. One was exposed for an hour to good sunshine, whilst the other was carefully kept in the dark. At the end of this time, a solution of the protosulphate of iron having been made in the dark, ten drops of it were added to each solution of silver. The one which had been exposed gave *immediately* a copious precipitate of silver, whereas the other was only rendered slightly turbid, and was some minutes before it precipitated. After having stood eight or ten minutes no difference could be detected in the quantity of silver precipitated in either phial.

Acetate of mercury was used in the place of the acetate of silver, and the difference between the actinized solution and the other, on the addition of the iron salt, was very striking.

The two salts, acetates of silver and mercury, were mixed (they had been used, combined rather successfully, in a photographic process of some interest). One portion was exposed in a large test-tube carefully corked, and another portion was protected from all light in a bottle. The exposure in this case was from two to three hours, but during that time there was not more than half an hour's good sunshine. By the light of a taper an equal quantity of the sulphate of iron was added to each. In about three minutes the solution which had been exposed appeared a little disturbed, small specks were seen to form in various parts of the fluid, and these rapidly increasing in size and assuming star-like shapes, fell heavily. At the expiration of an hour a dark and bulky precipitation was formed, but in the unexposed solution the precipitate was but little and of a light gray colour. In about two or three hours a coating of white metal was formed in two well-defined stripes along the tube which had been under solar influence; one on the side directly facing the sun, and the other on the other side of the tube, but along a line, upon which I found by subsequent experiment the rays were concentrated, by the form and refractive power of the media—glass and metallic solution—through which they had to pass. That these lines were due to the action of the solar rays was proved by placing a piece of blackened paper around a tube, as marked in the figure, which effectually prevented the metallic deposit over the space it covered. This deposit is somewhat capricious in its formation. The experiment has been often repeated, but although the precipitation was invariably as described, it frequently happened that no metal was deposited along the glass.

Sulphate of iron in solution was found to acquire the

same property by exposure as the other salts above-named. 30 grs. of this protosalt were dissolved in an ounce and a half of water. It was then divided into two portions, one of which was exposed for an hour to sunshine. 100 grs. of each solution were carefully weighed into test-tubes, and the same weight of a solution of nitrate of silver made in the dark, was added to each. As quickly as possible the precipitates were collected, washed, dried and weighed. The precipitate produced immediately by the iron solution which had been actinized weighed 2·8 grains, whereas the precipitate by the unexposed solution weighed 0·7 grain. These results are the mean of six experiments.

Two test-tubes had 120 grains of an actinized solution of nitrate of silver weighed into them, and into two others was put the same quantity of a like solution which had not been actinized. Four other tubes held the same weights of solutions of the protosulphate of iron, two of them actinized, the others not so. They were mixed in the following order, and the precipitates collected immediately from each were as stated:—

1. Actinized silver with actinized iron . 0·5 gr.
2. Unactinized silver with unactinized iron 0·7 ...
3. Actinized silver with unactinized iron 1·0 ...
4. Unactinized silver with actinized iron 1·5 ...

Considerable difficulty arises from the length of time which must necessarily elapse before the precipitates can be removed from the solutions. In all cases I find that after some little time the conditions required to effect a precipitation are established, and in both kinds of solutions it then proceeds without any apparent difference. It would appear from the above results, which are the mean of many experiments, that when both solutions are brought into the same actinic condition they do not precipitate more freely than those do which have been kept in the dark. It appears to be necessary that the actinic states should be dissimilar to ensure the production of these curious phænomena, which evidently point to some law of chemical action which has not yet been made the subject of study.

Bichromate of potash, it is well known, is decomposed by the agency of the solar rays when in contact with organic matter. A solution of this salt spread upon paper forms a photographic agent of some interest. The paper, which is of a fine yellow colour when first prepared, becomes brown upon exposure to the sunshine, from the chromic acid of the salt being acted upon by the organic matter of the paper. A similar change takes place, to a certain extent, in solutions of this salt in distilled water, when exposed in clear glass ves-

sels, for some time, to bright sunshine. The evidence we have of this is the gradual formation of minute bubbles of air, which are redissolved, and the progressive increase of free chromic acid in the solution, which may be detected by any of the usual methods.

A combination of the bichromate of potash and of sulphate of copper, either on paper or in solution, exhibits the above change very clearly, in the gradual formation of a chromate of copper of a peculiar character, which, although brown at first, becomes nearly white by prolonged exposure to solar influence; indeed, upon paper the whiteness is quite complete. Some very remarkable changes have been detected in combinations of these salts, which will be made the subject of a future communication.

Actinic Influence on Electro-chemical Action.

Some years since, when endeavouring to discover the chemical action exerted by the sun's rays on the iodide of silver, I was induced to form some small galvanic arrangements, a description of which and the results of my experiments, I published in the Philosophical Magazine for October 1840. As these experiments bear strongly on my present researches, I venture to extract a passage or two from that paper.

"In a watch-glass, or any capsule, place a little solution of silver; in another, some solution of any hydriodic salt; connect the two with a filament of cotton, and make up an electric circuit with a piece of platina wire; expose this little arrangement to the light, and in a very short time it will be seen that iodine is liberated in one vessel, and the yellow iodide of silver formed in the other, which blackens as quickly as it is formed.

"Place a similar arrangement to the above (31.) in the dark, iodine is slowly liberated. *No iodide of silver formed, but around the wire a beautiful crystallization of metallic silver.*

"A piece of platina wire was sealed into two glass tubes; these when filled, the one with hydriodate of potash in solution, and the other with a solution of the nitrate of silver, were reversed into two watch-glasses containing the same solutions, the glasses being connected by a piece of cotton. A few hours of daylight occasioned the hydriodic solution in the tube to become quite brown with liberated iodine; a small portion of iodide of silver was formed along the cotton, and at the end dipping in the salt of silver. *During the night the hydriodic liquid became again colourless and transparent, and the dark salt along the cotton became yellow as at first.*"

I have resumed this inquiry under modified conditions,

but the results have been invariably of a similar character to the above. I shall for the present merely describe two sets of experiments, from which I draw these conclusions:—

1st. That electro-metallic precipitation is prevented by the influence of the sun's rays.

2nd. That light is not the retarding agent, but that the exercise of electrical force is negatived by the direct influence of actinism.

I placed in a test-tube a strong solution of nitrate of silver; in another tube, being closed at one end with a thin piece of bladder, I placed a solution of iodide of potassium; this was supported in the solution of nitrate of silver by being fixed in a cork, and a piece of platina wire was carried from one solution into the other. An arrangement of this kind was kept in the dark; iodine was liberated in the inner tube, and a crystalline arrangement of metallic silver was formed around the platina wire in the outer one. Another was placed in the sunshine; iodine was liberated in the dark, but no silver was deposited.

Having exposed the above solution to the sunshine of July during a long day, the tube was placed in a dark cupboard, but the actinic influence which had been exerted on the solution of silver had produced a permanent change in its condition; after several days no trace of any metallic deposit could be detected, but the whole of the iodine again entered into combination, whereas this was not the case in the unexposed glasses.

In the inner tube I placed the solution of silver, and in the outer one the hydriodate of potash. One arrangement was kept in the dark, the other was exposed to good sunshine. In both instances the liberated iodine gave an intense yellow to the solution, and in both cases the quantity of metallic silver deposited was precisely the same.

This yellow fluid being analysed by the prism was found to obstruct all the rays above the green, whilst it permitted the permeation of the yellow and orange rays in great quantity and power. It is therefore evident that the luminous rays of the solar spectrum have no power in retarding electro-chemical action.

I submit these details of experiments in a new and important branch of science to the Chemical Society, knowing that they form but a very imperfect account of an extensive series of phænomena, but I do so with the hope of being enabled eventually to render my contributions more comprehensive.

March 17, 1845.—The President in the Chair.

The following presents to the Society's Library were announced:—

"Annals of Philosophy," 16 vols., from 1 to 16; "Bergmann's Essays," 2 vols.; "Henry's Chemistry," 2 vols.; from the London Chemical Society.

"Annuaire de Chemie, 1845, par MM. Millon, Reiset et Hoefer;" from the editors.

G. H. Makens, Esq., and H. M. Morgan, Esq., were elected Members.

The following papers were read:—

CXXXV. *On Brown Iron Ore. By* Lieut.-Col. P. I. Yorke.

SOME observations having led me to believe that the analysis generally assigned in systems of mineralogy to the crystallized hydro-oxide of iron really belonged to another substance, I undertook the following experiments to clear up the point.

When I made the experiments I had not seen the second edition of Dana's Mineralogy*, or the analyses of Kobell quoted therein, or I should probably have saved myself the labour. Although my results accord with those of Kobell, yet as it does not appear that any distinctly crystallized specimen has been analysed, and as the most interesting problem in mineralogy is the connection between crystalline form and composition, it may not be deemed superfluous if I submit my results to the Chemical Society.

A. *Crystallized Brown Iron Ore.*

The specimen was obtained from Restoomel mine near Lostwithiel. The specific gravity of the mineral, taken on a crystal weighing 2·504 grs., I found to be 4·37; when taken from the powdered mineral, in the manner described by G. Rose, it came out 4·22 to 4·24.

I annex figures of the forms of two crystals, and the measurements I have observed on them, together with those of similar angles obtained by Phillips and Levy. Levy makes the primary form a right rhombic prism of 95°·14, the ratio of whose terminal edges is to that of the lateral edges as 10 to 9†; and I have followed this author in the choice of the planes assumed as primary.

Fig. 1. agrees perfectly with the view that the primary form is a right rhombic prism; but with the crystal fig. 2. I met with a difficulty, inasmuch as I obtained as the inclination of *g*, on a plane apparently corresponding to *h*, fig. 1, the angles

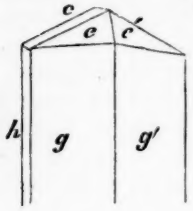
* A System of Mineralogy, by James Dana, 2nd edit., New York and London, 1844.

† *Description d'une Collection de Minéraux formée par M. H. Heuland*, par A. Levy. Londres, 1837. vol. iii. p. 155.

115° 40′, and with g' on the other side 114° nearly. I believe this is owing to there being in reality two very narrow planes, $i\ i'$, as I have represented them in fig. 2, meeting at a very obtuse angle, and to my catching the reflexion from one plane only. Could it be from a cause of this kind that G. Rose has referred this substance to his fifth system of crystallization?* I hope an experienced crystallographer may be induced to examine this crystal.

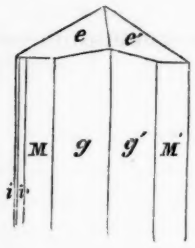
Composition.—Some preliminary experiments satisfied me that the substance consisted of red oxide of iron, oxide of manganese and water, with small but variable quantities of silica. I could not detect any phosphoric acid or alumina.

Fig. 1.



	W. Phillips †.	P. I. Yorke.
g on g' . .	130° 40′	130° 27′.
g on h . .	117° 50′	114° 46′.
c on h . .	121° 45′	121° 34′.
g on e . .	129° 30′	129° 26′.

Fig. 2.



	Levy ‡.	P. I. Yorke.
M on M′ . .	95° 14′	96° 0′
g on i' . . .		115° 42′?
g on i . . .		114°?

The most brilliant and perfect planes are $g\ g'$.

Quantitative Analysis.

1. 100 parts lost by ignition 10, and left undissolved, when acted on by muriatic acid, 2·61 of silica.

2. 12·16 grs. of picked crystals free from quartz yielded—

		In 100 parts.
Silica	0·035	0·28
Water	1·225	10·07
Red oxide of iron . . .	10·89	89·55
Oxide of manganese . .	0·02	0·16
	12·17	100·06
Excess . .	0·01	

The silica obtained is probably an admixture only; abstracting the silica, the following gives the result of experiment compared with theory:—

* *Elémens de Crystallographie*, par G. Rose, traduit par V. Regnault, p. 261 (18). † Crystals from the neighbourhood of Bristol.

‡ Crystals from Botallack, Cornwall.

		Atomic Weight.		In 100 parts. Theory.	Experiment.	
Fe_2O_3	=	80	=	89·89	89·81	89·97
					Mn_2O_3 0·16	
HO	=	9	=	10·11		10·10

This formula ($Fe_2O_3 + HO$) agrees with that obtained by Kobell from substances designated as nadeleisenerz, goethite and lepidokrokite *: the first is a name given by Breithaupt to the crystals found in the neighbourhood of Bristol, which have been described by W. Phillips; the specimen examined by Kobell was from Oberkirchen in Oldembourg; it was crystallized, but the crystals were not measurable. This is undoubtedly the same species that I have just described. Under the second name is included a substance of the same composition apparently as the first, but from the observations of Rose it seems doubtful whether it has the same crystalline form †. It is under the name of goethite, however, that our mineral of Lostwithiel, &c. appears in Dana's work. I may now remark, that as the composition of this substance is perfectly analogous with that of manganite ($Mn_2O_3 + HO$), so are the crystals plesiomorphous; the primary form of manganite being a right rhombic prism of 99° 40′, and the ratio of its terminal to its lateral edges is as 25 to 21 (Levy). The secondary planes also, which appear on the figures 1 and 2, are found on the crystals of manganite, as may be seen by examining the figures of that mineral in the works of Phillips and Levy.

Kobell comes to the conclusion that there are in nature two hydrates of the red oxide of iron, viz. $Fe_2O_3 + HO$, and $2\,Fe_2O_3 + 3\,HO$: the first very rare, the second common. My observations lead me to believe that the first is by no means uncommon in England, as appears by the following examination of brown iron ore from different localities.

α. Compact brown iron ore accompanied by very minute crystals from the Forest of Dean. Specific gravity obtained from a fragment 4·11. It contained 1 per cent. of silica, and deducting this lost 9·8 per cent. by ignition.

β. Fibrous brown iron ore, part of a stalactite, from the same locality as the last; sp. gr. 4·22: loss by ignition 9·41 in 100.

γ. Fibrous brown iron ore from Cornwall; sp. gr. 4·19; loss by ignition 10·24 in 100.

These specimens, then, all appear to belong to the same species, $Fe_2O_3 + HO$.

* *Annales des Mines*, 3d Ser. vol. xi. p. 493.

† According to Levy the forms are not incompatible.—Vol. iii. p. 161.

B.

I then examined a specimen, also from Cornwall, which was partly compact and breaking into smooth splintery fragments, and partly earthy. The sp. gr. taken on a fragment = 3·71, taken from the powdered mineral = 3·98. 8 grs. dissolved in muriatic acid and examined for alumina gave a barely perceptible precipitate of that substance; I could not detect any phosphoric acid, but obtained a trace of a white malleable metal, whose sulphuret was soluble in hydrosulphuret of ammonia, and which appeared to be tin. It lost 14 per cent. by ignition. The following was the result of analysis made on 10·99 grs.:—

		In 100.
Silica	0·26	2·42
Water	1·57	14·28
Sesquioxide of iron	9·03	82·16
... of manganese . .	0·124	1·13
Trace of alumina of tin, loss .	0·006	
	10·99	99·99

Deducting the silica and using the same atomic numbers as before, $2Fe_2O_3+3HO$ would contain in 100,—

	Theory.		Experiment.
Peroxide of iron.	85·57	84·32 Ox. mang. 1·15	85·47
Water	14·43		14·53
	100·		100·

This, then, is the substance called limonite by Beudant, and to this species belongs the analysis of D'Aubuisson commonly attached to the crystallized mineral first described.

C.

I have also examined a specimen of fibrous brown iron ore, which was ticketed "Brauner Glasskopf" from Wansiedel. This specimen was covered externally by a blackish, brilliant substance about one-tenth of an inch thick, which separated from the body of the specimen on hammering it, and broke off in small, brilliant, concretionary masses, which might at first sight be mistaken for crystals. The powder of this substance was of a purplish red. It lost 5·3 per cent. of its weight by ignition.

19·835 grs. of the body of the specimen which had a fibrous structure, separated from the external coating, yielded on analysis—

		In 100.
Silica	0·29	1·46
Water	2·46	12·42
Red oxide of iron	17·02	85·80
$\frac{2}{3}$ Oxide of manganese . . .	0·26	1·30
Excess	0·20	
	19·835	100·98

This analysis agrees with the hypothesis that the substance is composed of single equivalents of the two mineral compounds just described, but it would be altogether premature from this single result to assume the existence of such a definite compound.

Indeed these experiments seem to me to lead rather to the notion that all the brown iron ores having a crystalline structure, including the fibrous varieties, belong to the species first described, and are composed of 1 atom of peroxide of iron and 1 atom of water.

D.

A solution of persulphate of iron was precipitated when boiling by a solution of carbonate of soda; the precipitate was washed with large quantities of hot distilled water and then dried at 212°. It was of an orange-brown colour, and had a specific gravity of 3·77.

To ascertain the degree of purity of this substance, 20 grs. were dissolved in muriatic acid, and chloride of barium added; this gave a precipitate which, when ignited, weighed ·3 gr. = ·1 sulphuric acid. 20 grs. were also dissolved in muriatic acid, and precipitated by caustic ammonia; the liquid filtered, evaporated to dryness, and the residue ignited, weighed ·298 gr., consisting of sulphate of soda mixed with the oxides of manganese and iron. From these experiments it would appear that the substance cannot contain more than about 1 per cent. of impurity derived from its mode of preparation. When ignited in a platina crucible it lost 14·05 per cent. by one experiment, and 14·15 by a second; it was therefore $2\,Fe_2O_3 + 3\,HO$.

A portion of this substance contained in a test-tube was placed along with a thermometer in a bath of fusible metal; it began to give off water at about 260°; it was kept at a little below 400° till no more water was given off; the remainder then lost by ignition 10 per cent.; it was therefore converted into $Fe_2O_3 + HO$ at that temperature. When the temperature of the bath was raised to 500°, or a little higher, more water was given off, and by weighing it appeared that nine-tenths of the quantity of water contained in the substance could be driven off at that temperature, but not the whole.

A portion of the native sesquihydrate (B) behaved much in the same manner, and appeared to be converted into $Fe_2O_3 + HO$ at a temperature between 380° and 400°.

The native protohydrate (A B) heated to 512° did not lose more than $\frac{3}{10}$ths per cent., this was probably hygrometric. It begins to give off its water however at a temperature considerably below red heat, which is visible by daylight.

CXXXVI. *Observations on the Action of Animal Charcoal.* By Robert Warington, *Esq.*

ABOUT twelve months since a friend requested that I would undertake the performance of an experiment for him, which, if successful, he considered might prove of importance. The idea had occurred to him in passing one of the large breweries, that, from the greatly increased demand for pale ale, such as is exported to India, as a beverage for home use, it would be practicable to discharge the colour from the ordinary beer by artificial means, and thus obtain the desired object. What rendered this, he said, the more important, was the difficulty he had heard expressed by persons interested in the matter, in preparing an article sufficiently pale for the purpose of sale, the malt employed requiring to be made expressly for this quality of beer. To effect this desideratum, he considered that all that would be required would be to pass the fluid through a medium of animal charcoal, and that the ordinary amber colour of ale would be thus partially removed. I undertook to make his experiment for him, at the same time telling him that I thought the beer would be rendered very flat and the flavour much injured, but certainly not anticipating what followed. The method adopted, as presenting the least objectionable points to the successful attainment of the desired object, was to pass the cold ale through a stratum of animal charcoal placed on a paper filter, and to repass the filtrate through the same medium until the required effect was obtained; the ale operated upon was high-coloured, and had a bitter taste and the fine aroma of the hop. The colour was rapidly removed, but the ale was found on tasting extremely vapid and flat, and the whole of the bitter flavour was found to have been also abstracted. Not being prepared for this result, I was surprised at the rapidity of the action, and resolved immediately to carry on the investigation by substituting other and stronger bitters in the place of the hop. For this purpose a quantity of the ale which had previously had the flavour of the hop removed by charcoal was prepared, one portion of which was boiled with bruised gentian root

and another with the raspings of quassia wood, but on passing these decoctions when cold through the charcoal filter as before, the whole of the intense bitter flavour which they had imbibed rapidly disappeared.

It now occurred to me that this property of animal charcoal might be made of considerable utility to the chemist, as, from all our information up to the present time, it does not affect the active alkaline organic principles, and therefore should prove the means of separating the bitter of the hop and other materials from that of strychnia or morphia as contained in nux vomica or opium, it being frequently stated that some persons, vendors or makers of this common beverage, are in the habit of adding these and other materials in small quantities to their beer to give it a more intoxicating power. I therefore digested some nux vomica in coarse powder with a part of the ale prepared for the previous experiments, and on passing this when cold a great number of times through the charcoal the bitter flavour still remained, and hence I concluded at the time that my hypothesis was correct. Other engagements broke in on my experiments at this time, and prevented my prosecuting the investigation further.

About ten days since, however, I was recalled to this subject by some other experiments, and tried the effect of animal charcoal on the decoctions of some other astringent bitter substances, as oak bark, Peruvian bark (*Cinchona cordifolia*), and others, all of which had their flavour entirely removed. It may be as well to mention here, that in this second and also in a subsequent series of experiments the animal charcoal was added to the warm solution of the material under trial, and they were digested together on a sand-bath until the full effect had taken place, after which the fluid was passed through a filter. The charcoal used was the ordinary bone-black of the sugar-refiner purified by digestion with hydrochloric acid, washed as long as any saline matter was abstracted, and then dried and heated to low redness. I then tested the extent of this extraordinary power of charcoal by submitting a decoction of aloes to its action, with the same results, the whole of the bitter flavour being removed.

I had proceeded thus far when I was referred by my friend Mr. Henry to a work published at Breslau in 1842, by MM. A. Duflos and A. Hirsch, entitled *Ökonomische Chemie*, where, under the article Beer at page 65, I found nearly all that I had observed described in a few words; namely, that the bitter of the hop, and of all other vegetables used as substitutes for it, as gentian, wormwood, &c., and even aloes, was removed by animal charcoal, but that the bitter of nux vomica, which is often made use of in England, was not affected.

On looking over my experiments, however, my attention was arrested by finding that the decoction of the bark of the *Cinchona cordifolia* had had the whole of its bitter removed. Now, on the grounds stated in the previous part of this paper regarding the active principle, this should not have been the case. I therefore took a small quantity of disulphate of quina, dissolved it by heat in distilled water, and then added the charcoal, and discovered that the whole of the bitter was removed in less than a minute. A solution of acetate of morphia was also submitted to the action of charcoal with a like result. A watery solution of strychnia was similarly affected, and this made it necessary to repeat my former experiment on nux vomica, which had been made on a cold solution and simply filtering it through the charcoal; it was now digested with the aid of heat, and the whole of its bitter flavour quickly disappeared. The statement of Duflos and Hirsch, on this point, is not therefore entirely correct.

To try the extent to which this abstracting power proceeds, 2 grains of disulphate of quina were dissolved in 2 ounces of distilled water, and animal charcoal gradually added in small quantities to the warm solution until the whole of its bitter flavour was removed; it was found that 12 grains of the charcoal had been required to effect this.

It becomes a matter of surprise that this power of animal charcoal has, as far as I am aware, never been observed before, notwithstanding the frequent and extensive employment which is made of this agent in the preparation of the vegetable alkalies, their salts, and a great variety of other substances of an organic nature, for which it is directed to be used for the purposes of discoloration in all our chemical works and pharmacopœias. Numerous analyses of organic substances, in which it has been employed, will also be open to error on the same grounds.

Before leaving this branch of the subject, I should refer to a paper, and I believe the only one that bears particularly on any of the previous statements, by Dr. Louis Hopff, in the 17th volume of the *Journal de Pharmacie*, p. 172, "On the property of Charcoal in destroying the bitter flavour of many bodies;" in which he gives a series of comparative trials with wood and animal charcoal at a temperature between 78° and 86° Fahr. on solutions of a specified strength, of the extracts of bitter herbs, woods, roots, barks, leaves, flowers and fruits.

I annex a few examples from this paper of substances which have formed the subject of experiment in the present communication, as I believe that the great discrepancies which will be noticed arise from the charcoal employed by Dr. Hopff not having been well prepared.

	After twenty-four hours.	After forty-eight hours.	After boiling.
Gentian ...	Had lost a little of its bitter.	Purely bitter.	Had lost very little of its bitter.
Quassia ...	Perhaps lost a little of its bitter.	As before.	Lost very little of its bitter.
Aloes	Perhaps a little changed.	A little changed.	As before.
Nux vomica	Very little changed.	Little changed, still very bitter.	Sensibly less bitter.

In a note the author says that the bitter of nux vomica disappeared entirely on agitating its solution with a great excess of animal charcoal.

By analogical reasoning I was led to try the effect of this agent on salts of inorganic constituents, and here a similar action was exerted. A large quantity of sulphate of magnesia was removed from its solution in water, as also of chloride of barium, sulphate of soda and other salts. The fact of sulphate of lime being removed from its solution has I find been already noticed by Payen and Graham.

On laying the preceding experiments before the Society, I stated that I proposed to carry on the investigation, but I have since met, in the number of the 'Chemist' for April, with a translation of a paper by M. Chevallier, "On the action of Animal Charcoal on Metallic Salts," in which he also proposes investigating its action on the *organic salts*. Had I been aware of the existence of this paper at the time, I certainly should not have brought my own experiments forward, and shall not continue the investigation until M. Chevallier has closed his researches. I can only express my regret that I should even thus far have anticipated his results.

March 31, 1845.—Anniversary Meeting.—The President in the Chair.

The following Report of the Council was read by the President, and subsequently ordered to be printed in the Society's Transactions:—

CXXXVII. *Annual Report of the Council.*

THE Council have the pleasure of reporting to the Society that the anticipations held forth in last year's report, of continued and increasing activity and usefulness on the part of our Members, have been fully justified by subsequent proceedings. Henceforth the Chemical Society will take its place among the other scientific institutions of the country; and as the rank which it will hold depends on the number and value of its published communications, a serious duty devolves on the Council to stimulate and encourage the zeal of the Members by every means in their power. Bearing in mind the rapid progress of chemical discovery, and the na-

tural wish of every contributor that no unnecessary delay should be interposed in the publication of papers, the Council (by pressing somewhat unreasonably on the time and good will of the Secretary) have been able to present to the Members during the last year Nos. 7, 8, 9, 10, 11, 12 of our printed Memoirs and Proceedings. The communications herein contained are forty in number, of which twenty-six are from the ordinary Members of the Society, nine from Associates, and five from foreign Members. They will be found to contain investigations in many cases of great value in the departments of light and heat, of electro-chemistry, of inorganic and organic chemistry, as well as many practical details of interest and utility. To particularize those which stand highest in importance would be an invidious undertaking, and is the less required, seeing that the documents themselves are already in your possession.

The usual Meetings of the Society have been well attended, and the vacancies in our numbers, produced by death and other causes, have been more than made up by new accessions. The entire number on our list last year was 168; our present number is 197, consisting of 88 resident, and 90 non-resident ordinary Members, 13 Associates, and 6 foreign Members. Our finances are in a satisfactory state, the income of the present year being 266*l.*, exceeding by 39*l.* that of the last year. Our domestic arrangements with the Society of Arts continue to our mutual satisfaction. Some additions have been made to our small Library by the presentation of works of standard value, and of periodical publications; and part of our income continues to be employed in the purchase of such English and foreign journals as are best calculated to exhibit the constant progress of science. Our collection of characteristic specimens of chemical substances has received several additions during the last year, but many more are wanted to enable the Council even to begin to form a list of deficiencies; at present all that can be said is, that contributions in this department are greatly desired, and will be very thankfully accepted.

The lapse of the last year has borne away from among us, by death, two of the original Members of the Society, Dr. Hope and Mr. Daniell; the former in advanced age, after a long life of activity, the latter in full intellectual vigour.

Thomas Charles Hope, M.D., was born at Edinburgh, 21st of July, 1766, being the son of Dr. John Hope, Professor of Botany in the University of that city. In 1787, being then in his twenty-first year, he was nominated Lecturer on Chemistry in the University of Glasgow on the death of Dr. Irvine; and two years afterwards was appointed Professor of Medicine in the same University conjointly with his uncle,

Dr. Stevenson. It was not, however, till 1793 that he began to lecture in either of these departments, being occupied during the interval in foreign travel and in preparing himself for the due discharge of his professional duties. In 1795, Dr. Black, being about to retire from the Chair of Chemistry in the University of Edinburgh, associated Dr. Hope with him as his coadjutor in the last course of chemistry which he gave, and thus potentially recommended him to the electors as his successor. From that time to the year 1843, being a period of forty-nine years, Dr. Hope devoted himself most assiduously to the delivery of an annual course of scientific chemistry during the University session; and occasionally of a more popular course during the summer months, exhibiting the application of this science to the various arts of civilized life. Nearly contemporary with the outset of Dr. Hope's career was the invention of the theory and nomenclature to which Lavoisier has given his name, and of which the simplicity and systematic consistency so admirably adapts it to use in the lecture-room. Dr. Hope had the good sense to adopt from the first the novel views and terminology of the French philosopher, and thus bespoke for his lectures a popularity and interest which was most amply confirmed by the unexampled success of his illustrative experiments, and the clear simplicity of his language, indicative of a complete mastery of the subjects on which he treated.

To be at the same time an admirable lecturer and great discoverer requires a conjunction of talents granted only to one man in an age, and certainly Dr. Hope was not that man; but in the few original investigations carried on by him he acquitted himself with credit, and his name is advantageously associated with the discovery of the alkaline earth strontia, and with the determination of the temperature at which water acquires its greatest density.

It is worthy of remark, as a singular instance of vigour both of mind and body, that Dr. Hope was prevented by illness from discharging his professional duties not more than six days during the whole time of his connexion with the University of Edinburgh, and that he died, so to speak, almost in harness, having the happiness of surviving scarcely a year his retirement from office, being at the time of his death, on the 13th of June 1844, in the seventy-eighth year of his age.

John Frederic Daniell died suddenly of an attack of apoplexy at the apartments of the Royal Society, while attending a meeting of the Council of that body, of which he was a distinguished member. His earliest contributions to science were made through the Quarterly Journal of Science and Art, and relate chiefly to the subjects of meteorology and crystallization. In 1814 he was elected a Fellow of the Royal

Society. In 1820 he published his description of a hygrometer, which was followed in 1823 by his Meteorological Essays, of which a second edition appeared in 1827. The medal of the Horticultural Society was awarded to him in 1824, for his paper on Climate considered with reference to Horticulture. A description of his very ingenious pyrometer appeared in 1830, together with a list of the melting-points of metals ascertained by means of it. The value attached by the Royal Society to this communication was shown by their voting to him in 1832 the Rumford medal, directed by the founder of the bequest to be given from time to time for the most useful discoveries in relation to heat. In 1830, King's College, London, was founded, and Mr. Daniell was appointed Professor of Chemistry in that institution. From this period most of the time that could be spared from his official duties was devoted to the investigation of electro-chemistry. To this interesting department of experimental science he consecrated his energies and industry, and was rewarded with the discovery of many new and important facts. The first of his electrical papers was published in 1836, in which he describes his constant battery, and points out the cause of the continual decline of power in batteries of the usual construction. For this paper he received in 1837 the Copley medal. In 1839 he published his Introduction to Chemical Philosophy, in which the subjects of light, heat, galvanism or electro-chemistry, and the general laws of chemical attraction are discussed at length, and show to what departments of experimental philosophy his attention was principally directed. In the same year appeared his first essay on the Electrolysis of Secondary Compounds, in which he shows that when saline solutions are electrolyzed, one equivalent of water and one of the salt are simultaneously decomposed for each equivalent of zinc consumed in the battery: hence he is led to consider the decomposition of water as only a secondary phænomenon resulting from the action on it of the disengaged elements of the salt. This essay was followed in 1840 by a still more extended series of research on the same subject, by which the binary theory seems to be established on experimental evidence. For these papers, in 1842, he received the Royal medal. In 1839 he was elected Foreign Secretary to the Royal Society, and on the establishment of the University of London was appointed Examiner in Chemistry. During the last year of his life he was engaged in revising his Meteorological Essays, and had nearly completed his undertaking when that and all his other designs were brought to an abrupt conclusion by his sudden and regretted death.

The audited report of the Treasurer was also submitted to the Society.

AUDITORS' REPORT.

Dr. ROBERT PORRETT (*Treasurer*), *in Account with the Chemical Society of London.* *Cr.*

1844.		£	s.	d.
March 25.	To Balance from last Account	322	8	5
1845.				
March 25.	To Subscriptions and Compositions since received.....	206	0	0
		£528	8	5

1844.		£	s.	d.
April 4.	By payment for Bookbinding	1	4	9
20.	——— for Test-tubes	0	6	0
June 20.	——— for Rent to Society of Arts	25	0	0
24.	——— of Poundage, &c. to Collector	4	14	0
Nov. 18.	——— of Gratuity to Servants of Society of Arts	1	0	0
1845.				
Feb. 3.	——— to R. and J. E. Taylor for Printing, from May 1843 to September 1844 ...	140	17	1
March 29.	——— for Scientific Journals and Books, English and Foreign.....	14	19	6
29.	——— for Stationery, Account-books, Postage Stamps, Envelopes, &c.	2	12	9
29.	By Balance to his Debit in new Account	337	14	4
		£528	8	5

London, 29th March, 1845.

R. PORRETT, *Treasurer.*

We have examined the above Account and find it correct,

JOHN PHILLIPS,
GEORGE D. LONGSTAFF, } *Auditors.*

The following Gentlemen were then elected Officers and Council for the ensuing year:—

President.—Thomas Graham, Esq.

Vice-Presidents.—Arthur Aikin, Esq.; William Thomas Brande, Esq.; John Thomas Cooper, Esq.; Thomas Thomson, M.D.

Treasurer.—Robert Porrett, Esq.

Secretaries.—Robert Warington, Esq.; George Fownes, Esq., Ph.D.

Foreign Secretary.—E. F. Teschemacher, Esq.

Council.—Benjamin Babington, M.D.; William John Cock, Esq.; Warren De la Rue, Esq.; William Gregory, M.D.; James F. W. Johnston, Esq., M.A.; Robert Kane, M.D.; W. B. Leeson, M.D.; W. Hasledine Pepys, Esq.; Richard Phillips, Esq.; Joseph D. Smith, Esq.; John Stenhouse, Esq., Ph.D.; James Lowe Wheeler, Esq.

The thanks of the Society were severally voted to the President, Secretary, Officers and Council for their exertions during the past year. Numerous interesting Chemical objects were exhibited to the Members by Messrs. Graham, Warington and De la Rue.

April 7, 1845.—The President in the Chair.

Lieut.-Col. Yorke presented specimens of the Brown Iron Ores, which had formed the subject of his paper, to the Society's Museum; as also of Crystallized Oxide of Lead formed on Metallic Lead by the conjoined action of air and water.

Mr. Charles Button presented 8 volumes of old and scarce chemical works to the Library.

Henry Smith, Esq., and Alexander R. Arrott, Esq., were elected Members; and Mr. William Johnson an Associate of the Society.

The following papers were read:—

CXXXVIII. *On Styrole, and some of the products of its decomposition.* *By* Dr. John Blyth *and* Dr. Aug. Wilhelm Hofmann.

THE class of bodies comprehended under the general name of Balsams has not been forgotten in that active investigation of organic bodies to which chemists have with predilection devoted themselves, since the discovery of easier and securer methods of investigation have removed the chief difficulties. An examination of these substances was indeed highly desirable, as the knowledge of them derived from older works no longer corresponded to the present state of the science. The earlier investigations of these substances were purely qualitative; everything crystalline and which united with bases was benzoic acid; those, on the other hand, which did not enter into combination were described as camphor. If, on distillation, a volatile fluid body was obtained, it was considered sufficient to state that the substance contained also a volatile oil.

Since the discovery of the potash apparatus has introduced an entirely new mode of investigation, our knowledge on these points has considerably augmented. The labours of Fremy, Plantamour, Simon and Deville, are rich in interesting results.

Along with the proper balsams of Peru, Tolu, &c., there is also known in commerce a material whose extraction is uncertain, called liquid storax (*Styrax liquidus*), which, from its properties, is closely allied to this class of substances. Fluid storax has already been the subject of several investigations. The earliest known to us is that of Bouillon-Lagrange*. It contains no results at all deserving of notice. He considered the crystalline acid present in storax as benzoic acid. More lately, Bonastre† communicated observations on fluid storax. He investigated a crystalline deposit which had been formed in an alcoholic solution of the balsam long kept. These crystals, which Bonastre took at first for benzoic acid, were insoluble in cold and hot water, but soluble in alcohol; the solution had no acid reaction. To this indifferent crystallizable body he gave the name styracine. He found the same substance, along with many others, again in an investigation of the American Copal‡, a balsam which in many points resembles styrax.

The most complete investigation of fluid storax we owe more lately to Edward Simon§. This chemist first showed that the acid found in the balsam, and which had been hitherto taken for benzoic acid, possessed all the properties of cinnamic acid. An analysis of the silver salt made by Marchand‖ put this beyond a doubt. Simon gave also some fuller details on the substance named styracine by Bonastre, and finally he examined the oil obtained from fluid storax by distillation with water, and which in its properties was quite different from that prepared by Bonastre from the Copal balsam. To this oil from storax he gave the name styrole.

The investigation of this chemist is rich in interesting observations; on the other hand it contains in proportion but few analytical determinations. From the analyses of Marchand, Simon gives the composition per cent. of styrole and styracine, without however at all attempting to give rational formulæ. The determination of such formulæ was however

* *Ann. de Ch. et de Phys.*, 1st ser., t. xxvi.

† *Journ. de Pharm.*, t. xiii. p. 149. 1827.

‡ *Journ. de Pharm.*, t. xvii. p. 338. 1831; and *Mag. für Pharm.*, Von Gieger und Liebig, Bd. xxxvi. S. 90.

§ Liebig's *Annal.*, B. xxxi. S. 265.

‖ *Journ. für Prakt. Chem.*, B. xvi. S. 60.

of much interest, as only by these could the relations of the compounds to other groups be shown. To fill up this blank, we undertook, at the request of Prof. Liebig, to make some inquiries in this direction. These were performed in the laboratory of Giessen, and, we need scarcely add, that during their course we were assisted by his advice.

We commence with the description of the oil of storax.

Styrole.

1. *Preparation.*—The material which we employed for the preparation of styrole was the common commercial "liquid storax." It possesses a dark gray colour, and at the temperature of summer is of a soft consistency, which allows it to be drawn into threads. At a low temperature (0° C.) it is hard and brittle. It has a highly aromatic odour, and is so rich in oil, that it can be pressed out with the fingers. Fluid storax oil can be obtained by distilling the balsam with water; but, as the latter contains also free cinnamic acid, it is more advantageous to add an alkali. For this purpose we followed Simon in employing carbonate of soda, in his proportions of 14 lbs. of crystallized soda to 20 of storax. We found that the half was quite sufficient.

The distillation was conducted in a copper retort with a gentle heat; the watery vapour loaded with oil was directed through a serpentine tube. In this way a milky-coloured water distilled over, on the surface of which the oil collected in a transparent, slightly yellow layer. We have submitted to distillation in the above method about 70 lbs. of storax. The material we employed was not all received at the same time, and gave very different amounts of oil. In the first operation we obtained 12 oz. of styrole out of 41 lbs. of storax. A later preparation, in which 27 lbs. of the balsam were employed, gave scarcely more than 3 oz. This difference arises, as Simon has already remarked, from the age of the balsam, as the styrole experiences in time a peculiar change. To this point we shall return later.

The volatile storax oil, as it is obtained by distillation, contains a small quantity of water, from which it can be easily freed by remaining over fused chloride of calcium. The fluid deprived in this way of water can be regarded as pure styrole, although it still possesses a shade of yellow. To obtain it quite colourless, it must again be submitted to distillation.

In this operation a peculiar phænomenon is observed, which was first indicated by Simon. When styrole is heated in a tubulated retort in which a thermometer is placed, a

quantity of vapour is evolved at 100° to 120° C. At 145¾° the fluid begins to boil, and there distils over a clear, oily and beautifully iridescent fluid. For some time the thermometer remains stationary at the above temperature, then begins suddenly to rise so fast, that it must quickly be removed from the retort. The portion left behind has now completely changed its character to a thick, tenacious substance, through which the bubbles formed at the bottom of the vessel force their way with much difficulty to the surface. From this period scarcely any more oil distils over, and, on allowing the retort to cool, its contents become a solid transparent glass. The quantity of this solid residue is variable: it amounts sometimes to a third of the oil employed. We shall return to this point afterwards. The product of the distillation is perfectly pure styrole.

2. *Properties of Styrole.*—This body is in the form of a colourless, transparent fluid, of a burning taste and peculiar aromatic odour, resembling a mixture of benzole and naphthaline, which adheres tenaciously to linen. At a temperature of 20° C. it neither solidifies nor loses any of its extreme mobility. Exposed however to a mixture of solid carbonic acid and æther, it solidifies instantaneously into a beautiful white crystalline mass. It is in the highest degree volatile, and evaporates at all temperatures; the oily spots made by it on paper disappear after a few seconds. The boiling-point lies, as already stated, about 145¾° C. This same temperature was found in several trials. A wick dipped in styrole burns with a brilliant, smoky flame. Its vapour can be passed without decomposition through a red-hot tube.

Styrole is lighter than water: its specific gravity at the ordinary temperature of summer is 0·924. It disperses and refracts the rays of light in the highest degree. Its coefficient of refraction is for the red rays 1·532.

It mixes in all proportions with æther and absolute alcohol. Spirit of wine dissolves less according to the proportion of water it contains. It is soluble in pyroxylic spirit, acetone, bisulphuret of carbon, fat and æthereal oils. Water dissolves only a small proportion, but still sufficient to give it the burning taste and odour of the oil. The amount of water which can become mixed with the oil is equally small.

Styrole shows no reaction on vegetable colours. Like the æthereal oils, it dissolves by the aid of heat a large proportion of sulphur, which, on cooling, is deposited in the form of large prisms. Phosphorus is likewise soluble in hot styrole, from which it also crystallizes. Caoutchouc swells up by the aid

of heat in this substance; only a small portion however is dissolved.

3. *Composition of Styrole.*—We have already stated that on the occasion of Simon's investigation, Marchand analysed styrole. From his experiment it appears that this body consists of carbon and hydrogen, in the proportion of two of the former to one of the latter*. We have also analysed styrole, and our results confirm those of Marchand.

On combustion with oxide of copper, styrole prepared at two different periods gave the following numbers:—

I. 0·2722 grm. of styrole gave 0·9168 grm. of carbonic acid and 0·1935 grm. of water.

II. 0·4640 grm. of styrole gave 1·5745 grm. of carbonic acid and 0·3290 grm. of water.

Corresponding in the 100 parts to—

	I.	II.
Carbon . . .	91·86	92·54
Hydrogen . .	7·89	7·87

Theory requires—

			Mean of experiments.
2 equivalents Carbon†	= 150·0	92·30	92·20
1 ... Hydrogen	= 12·5	7·70	7·88
	162·5	100·00	100·08

The above experiments leave no doubt as to the relative amount of the carbon and hydrogen, but give no idea of the absolute number of equivalents of the elements in the equivalent of styrole; or, in other words, lead to no conclusion as to the formula of the compound. This point it was however very desirable to ascertain, as we already possess two bodies, benzole and cinnamole, which have the same composition in the hundred parts.

The determination of a chemical formula for styrole was attended with some difficulty. Like benzole and cinnamole, this body formed no direct compounds, if we do not consider here the products obtained by the action of chlorine and bromine; in the case of the former substances, however, their formulæ were in a certain measure given by their origin

* The volatile oil which Bonastre (*Journ. de Pharm.*, t. xviii. p. 344) obtained from the Copal balsam is certainly a totally different carbo-hydrogen from styrole. Henry and J. Plisson (same Journal, p. 451) found its composition to be—

Carbon	= 89·25
Hydrogen	= 10·46
Oxygen	= 00·29
	100·

This oil is also distinguished from styrole by becoming solid at 0° C.

† Carbon = 75. Hydrogen = 12·5.

from benzoic and cinnamic acids, and could be controlled by a determination of the specific gravity of their vapours. The origin of styrole, on the other hand, is quite obscure, and the determination of the specific gravity of its vapour was no longer to be thought of after we had observed the peculiar metamorphosis produced by the action of heat.

There remained therefore no other way to arrive at a proper formula than by studying the products of its decomposition. As we had already some information from Simon on this point, it appeared desirable to follow the same way. In the course of this memoir it will be seen that we were led to adopt $C_{16}\ H_8$ as the formula of styrole.

4. *Products of the Decomposition of Styrole. Action of Nitric Acid.*—In its physical properties styrole is closely allied to benzole and to benzoëne (toluine of Berzelius), lately discovered by Deville* as a product of the dry distillation of Tolu balsam. The interesting results obtained by Mitscherlich, and later by Deville, by the action of nitric acid on the above-named bodies, and particularly the remarkable transformation of nitrobenzide into aniline, observed a short time ago by Zinin†, indicated to us a method which promised to lead to a proper formula of styrole. Were a compound analogous to nitrobenzide to be obtained, or a base to be formed whose atomic weight could be easily determined, such data would at once lead to a knowledge of the proper constitution of styrole.

In the memoir already referred to, Simon has communicated some experiments on the action of nitric acid on styrole. He obtained a peculiar neutral body, which he named *nitrostyrole*, without however ascertaining its composition. Along with this body he observed the formation of benzoic and hydrocyanic acids.

Nitrostyrole.

The preparation of this substance is attended with difficulty. Notwithstanding a great number of experiments, we have not been able to find out a method to procure at will a considerable quantity of this body. According to Simon, storax oil must be distilled with nitric acid (but of what concentration is not stated) till it has become brown, and is completely converted into a resinous mass. After freeing it from nitric acid by washing, this resin is to be distilled with water, when the nitrostyrole volatilizes with the watery vapour.

By following the directions given by Simon, and employing

* *Ann. de Ch. et de Ph.*, 3rd ser., t. iii. p. 151; and *Ann. der Chem. und Pharm.*, Bd. xliv. S. 304.

† *Ann. der Chem. und Pharm.*, Bd. xliv. S. 286.

in the distillation ordinary nitric acid, we obtained indeed the peculiar substance named by him nitrostyrole, but in quantity bearing no proportion to the amount of oil employed. The oil is very slowly attacked by common nitric acid. On heating the mixture to boiling the styrole becomes of a yellow colour, but at the same time a large quantity of undecomposed yellowish oil distils over. Only after being five or six times poured back into the retort does it begin to change its character, by becoming heavier, more tenacious, and finally sinking to the bottom of the vessel. At this period the oil-drops which pass over with the water smell no longer of styrole, but possess a peculiar sharp odour of cinnamon, and violently attack the eyes. If the styrole has become quite brown and sunk to the bottom, it solidifies on the cooling of the retort into a resinous mass. The watery fluid above the resin, on the other hand, deposits a quantity of crystalline plates. On removing the crystals from the retort, washing the resin with water to free it from the nitric acid, and again heating to boiling the resin with water, the greater portion becomes dissolved, and there distils over a volatile matter possessing in the highest degree the odour of cinnamon. After a short time these oil-drops solidify in the retort. On allowing the retort to cool when no more of this substance passes over, the whole fluid becomes a crystalline mass. By long-continued distillation, a portion of this crystalline matter, which is, however, much less volatile than the nitrostyrole, also passes over into the receiver.

As already stated, the quantity of the volatile oil obtained was exceedingly small. Only after repeated operations, and at the sacrifice of several ounces of styrole, was a quantity prepared sufficient for analysis. It was separated by filtration from the fluid which distilled over with it, and after washing with water, which dissolves but a small proportion, again distilled with the vapour of water, and finally dissolved in boiling alcohol. On cooling, large beautiful prisms* crystallized from the solution, possessing the characteristic odour of cinnamon, and a sweet but highly burning taste.

The following results were obtained on combustion with oxide of copper, after the substance had been dried over sulphuric acid for several days:—

I. 0·2662 grm. of the crystals gave 0·6250 grm. of carbonic acid and 0·1190 grm. of water.

II. 0·1630 grm. of crystals gave 0·3885 grm. of carbonic acid and 0·0790 grm. of water.

* In the memoir of Simon exact measurements of these crystals are given from G. Rose.

III. 0·2787 grm. of crystals gave 0·1255 grm. of water.

IV. The nitrogen was determined by the method of Dumas, by burning the substance in an atmosphere of carbonic acid. 0·5088 grm. of crystals gave 48· cub. cent. of moist nitrogen at 19° C. and 327‴ barom.

These numbers correspond to—

	I.	II.	III.	IV.
Carbon . .	64·04	64·50		
Hydrogen .	4·96	5·38	5·00	
Nitrogen . .	.....	.....	.....	10·30

When we consider that the method of Dumas always gives an excess of nitrogen, we can from the above numbers deduce the following formula, $C_{16} H_7 NO_4$, giving per cent.,—

			Mean of experiments.
16 equiv. Carbon . .	1200·00	64·36	64·27
7 ... Hydrogen .	87·50	4·69	5·11
1 ... Nitrogen .	177·04	9·50	10·30
4 ... Oxygen . .	400·00	21·45	21·32
	1864·54	100·00	101·00

According to this formula, which will be further confirmed by the analysis of the bromine and chlorine compounds, the body investigated is analogous to nitrobenzide, which it resembles in many respects, and fully deserves the name of *nitrostyrole*, proposed by Simon.

If from this formula we deduce the composition of styrole, it must be expressed by $C_{16} H_8$, and the formation of nitrostyrole is shown in the following manner:—

$$\underbrace{C_{16} H_8}_{\text{Styrole.}} + NO_5, HO = \underbrace{C_{16} H_7 NO_4}_{\text{Nitrostyrole.}} + 2HO.$$

As to the properties of nitrostyrole, we have but little to add to the statements of Simon. This body is particularly characterized by its odour, which strongly irritates the eyes to tears, and by the manner in which it affects the skin, long contact with which produces a painful burning, and finally blisters.

On distilling a mixture of nitrostyrole and an alcoholic solution of potash, after most of the spirits have passed over, there are obtained red oil-drops, which are not nitrostyrole. From want of materials we have not investigated this body: it is probably a compound analogous to the *azobenzide* of Mitscherlich. An exact study of this reaction will certainly lead to interesting results, but there will be some difficulty in obtaining a quantity of substance necessary for such a purpose.

We further endeavoured to transform nitrostyrole into a base by the action of sulphuret of ammonium. This body

would have had the composition $C_{16} H_9 N$, and by treatment with oxidizing means would probably give compounds of the indigo series, perhaps *isatine*. We have hitherto, however, not succeeded in preparing it.

We have already stated, that by the treatment of styrole with nitric acid, there passes over, towards the end of the distillation, an oil which possesses in the highest degree the odour of nitrostyrole. This oil is nothing but a solution of nitrostyrole in several other fluid bodies, probably undecomposed styrole and some oil of bitter almonds. On exposing this mixture to a very low temperature ($-20°$ C.), it solidifies nearly completely into a crystalline mass, which can be separated from the adhering fluid oil by pressing in filtering paper: it is pure nitrostyrole.

Benzoic Acid.

The crystals which separate on the cooling of the watery fluid during the preparation of the resin for the formation of nitrostyrole, consist, according to the length of the distillation or the concentration of the nitric acid employed, either of benzoic or nitrobenzoic acid. In general we obtained a mixture of both.

To be quite certain on this point, we treated, in the repeated distillations which we undertook for the preparation of nitrostyrole, storax oil sometimes with quite dilute nitric acid.

By continuing the distillation for a considerable time, there passed over with the watery vapour a substance which condensed in the neck of the retort and in the receiver into a crystalline mass. This was dissolved in weak potash ley and boiled till all odour of nitrostyrole had disappeared. Acids produced in this alkaline solution a white crystalline precipitate, which was separated by filtration, washed, and dissolved in boiling water. From this solution large crystalline plates separate, which are identical with those deposited from the liquid above the resin (in the preparation of nitrostyrole), and which in every respect resembled benzoic acid. To remove every doubt, we formed benzole from it, and submitted the acid itself to analysis.

The following results were obtained by combustion with oxide of copper:—

0·3260 grm. gave 0·8230 grm. of carbonic acid and 0·1545 grm. of water.

The amount per cent. calculated from these numbers corresponds exactly to the formula $C_{14} H_6 O_4$, as is shown by the following statement:—

		Theory.		Experiment.
14 equiv.	Carbon . .	1050·00	68·85	68·85
6 ...	Hydrogen .	75·00	4·92	5·25
4 ...	Oxygen . .	400·00	26·23	25·90
1 ...	Benzoic acid =	1525·00	100·00	100·00

The transformation of styrole into benzoic acid is shown by the following equation:—

$$\underbrace{C_{16}H_8}_{\text{Styrole.}} + 10O = \underbrace{C_{14}H_6O_4}_{\text{Benzoic acid.}} + 2CO_2 + 2HO.$$

This equation merely represents the ultimate products of decomposition. It is, however, probable that an intermediate product precedes the formation of the benzoic acid. We have already mentioned a heavy oily liquid, which during the action of nitric acid on styrole condenses in the receiver. It contains, as stated, a large quantity of nitrostyrole; and also another fluid body, which we are inclined to consider as oil of bitter almonds. At least, at certain periods of distillation, the products acquired the strongest odour of that oil.

As the small quantity of the mixture we possessed excluded the possibility of a separation by distillation, we thought it might be possible to prove the presence of oil of bitter almonds by the formation of benzoine. For this purpose the mixture was treated, according to Zinin's method, with an alcoholic solution of potash and some cyanide of potassium*. We have, however, not been able to observe any crystals of benzoine, consequently the settlement of this point must be reserved for further investigation. The formation of oil of bitter almonds under the circumstances already mentioned would beside not have been very extraordinary. The investigations of Dumas and Peligot†, which were confirmed by Plantamour‡ and Simon§, have shown that cinnamic acid, treated by oxidizing means, produces hydruret of benzoyl before passing into benzoic acid. According to very recent observations of Cahours‖, oil of anise, before being finally changed into anisinic acid, is first converted into hydruret of anisyl, which stands in the same relation to the last acid as hydruret of benzoyl to benzoic acid.

Nitrobenzoic Acid.

If strong nitric acid, such as the commercial, has been employed in distillation with styrole, there are obtained, by the

* *Ann. der Chem. und Pharm.* Bd. xxxiv. S. 186.
† Ibid. Bd. xiv S. 59.
‡ Ibid. Bd. xxx. S. 349.
§ Ibid. Bd. xxxi. S. 271.
‖ *Compt. Rend.* t. xix. 795.

solution of the residue, crystals which possess all the properties of nitrobenzoic acid discovered by Mulder*. We have made several analyses of this acid and its silver salt, which, however, we consider we may pass over, as, after proving the formation of benzoic acid, the appearance of nitrobenzoic acid was easily explained.

Simon states that hydrocyanic acid is one of the products of the action of nitric acid on styrole: we have not observed the formation of this acid.

It has been already stated that the amount of nitrostyrole obtained was exceedingly small. We have modified the process for forming it in several ways, in order to obtain, if possible, this interesting body in larger quantities.

The analogy which exists between nitrostyrole and nitrobenzide, both in their mode of formation and properties, appeared to indicate the way to a more advantageous method of preparation. For this purpose we dropped styrole into fuming nitric acid, which formed with it a deep red solution, with great evolution of heat. Here also, even by the employment of artificial cold, the formation of red vapours could not be avoided. From the nitric acid solution water precipitated a yellow resinous substance of soft consistency, which possessed in the highest degree the characteristic smell of nitrostyrole. After washing with water till the greater part of the nitric acid was removed, the yellow mass was submitted to distillation with water. A quantity of nitrostyrole volatilized with the watery vapour, greater than was obtained in the former method, but still out of all proportion to the amount of oil employed. We were equally unfortunate in the treatment with fuming nitric acid, which had been previously saturated with deutoxide of nitrogen.

If a current of nitrous acid (NO_3) be passed through styrole when warm, a violent reaction takes place with the evolution of vapours, which possess the irritating odour of nitrostyrole; at the same time there is formed a peculiar odourless crystalline substance, insoluble in water, alcohol and æther. This compound we have not studied.

In this reaction, which is certainly very complicated, nitrostyrole is likewise formed in only very small quantities.

Action of Chromic Acid on Styrole.

On submitting to distillation a mixture of styrole, bichromate of potash, sulphuric acid and water, the greater portion of the styrole passes with the watery vapour undecomposed into the receiver. A reaction takes place only after the contents of

* *Ann. der Chem. und Pharm.* Bd. xxxiv. S. 297.

the retort have commenced to become solid; by continuing the distillation large crystals of benzoic acid collect in the receiver.

Action of fuming Sulphuric Acid on Styrole.

On mixing fuming Nordhausen sulphuric acid with styrole, a violent reaction takes place with the evolution of heat; the oil becomes tenacious, and assumes a dark colour. The addition of water produces the separation of a brown resinous mass. The fluid filtered from this substance gave, when treated with an excess of carbonate of baryta, a soluble baryta salt, which, however, could not be obtained in a crystalline form. The physical properties of these products, probably analogous to Mitscherlich's sulphobenzide and hyposulphobenzidic acid, are far from inviting to a nearer investigation.

Action of Bromine on Styrole.

Bromostyrole.—By the addition of bromine to the volatile oil of storax it becomes heated to boiling, and the evolution of hydrobromic acid always takes place. The oil is by this reaction completely transformed into a crystalline mass of a peculiar odour.

The formation of hydrobromic acid can be completely avoided by placing the flask in water and adding the bromine by drops. By waiting each time till the heat evolved has been removed, the product obtained is uniform.

The crystalline mass is insoluble in water, but communicates to it a highly peculiar penetrating odour and taste, which resemble a mixture of oil of citron and juniper. It is, on the other hand, very soluble in alcohol and æther. We have in vain endeavoured, by gentle evaporation of the æthereal solution, to obtain well-formed crystals. The boiling saturated alcoholic solution on cooling deposits the compound in the form of an oil, which covers the bottom of the vessel, and not unfrequently remains long fluid under the temperature at which it solidifies, until shaken, when it becomes solid. It fuses under boiling water. It is decomposed by an alcoholic solution of potash, bromide of potassium, and another compound containing bromine being formed.

The products submitted to analysis were of different preparations. Nos. I. and II. were formed directly by the treatment of styrole with an excess of bromine. The somewhat yellow substance was washed with spirits of wine till it appeared white, and after solution in the same menstruum was again precipitated by the addition of water, and washed with the same fluid till all trace of hydrobromic acid, which forms

in considerable quantity during the preparation, was removed. The substances employed in Nos. III. and IV. were made with great care; merely traces of hydrobromic acid were formed, which were also removed in the same manner.

The combustions, which were all made with chromate of lead, gave the following results:—

I. 0·3950 grm. of substance gave 0·5150 grm. of carbonic acid and 0·1155 of water.

II. 0·3095 grm. of substance gave 0·4085 grm. of carbonic acid and 0·0920 grm. of water.

III. 0·3650 grm. of substance gave 0·4085 grm. of carbonic acid and 0·1047 grm. of water.

IV. To determine the bromine, the substance was carefully mixed with caustic lime and heated to redness in a combustion-tube. The heated mass was then dissolved in nitric acid, filtered, and precipitated by nitrate of silver. Treated in this way there was obtained from 0·2668 grm. of substance 0·3805 grm. of bromide of silver.

These numbers correspond per cent. to—

	I.	II.	III.	IV.
Carbon .	35·85	35·99	36·23	
Hydrogen	3·23	3·27	3·18	
Bromine .	...	...	...	59·83

From which the following formula is deduced,

$$C_{16} H_8 Br_2;$$

giving per cent. the following numbers:—

16 equivts.	Carbon	=1200·00	36·85
8 ...	Hydrogen	= 100·00	3·07
2 ...	Bromine	=1956·61	60·06
		3256·61	100·00*

Action of Chlorine on Styrole.

Chlorostyrole.—By the treatment with chlorine there is formed a compound analogous to the bromostyrole. The chlorine compound is fluid. It is extremely difficult to prepare the chlorine compound pure. A stream of the gas passed through styrole is rapidly absorbed, without any evolution of hydrochloric acid, if the current be not too rapid, and the temperature kept low, at the same time that the influence of the direct rays of the sun be avoided. By long treatment the oil changes into a thick fluid, which is chlorostyrole. As soon as the evolution of hydrochloric acid indicates that no more styrole exists free, the action must be interrupted. The evolution

* The loss of carbon in Nos. I. and II. arose evidently from a mixture of another product richer in bromine. The evolution of hydrobromic acid in the preparation can only take place from such a cause.

of hydrochloric acid indicates that the decomposition is proceeding further, by the formation of products of substitution which contain fewer hydrogen equivalents than exist in styrole; whereas chlorostyrole is a simple compound of chlorine and styrole, or at least may be considered as such.

We have frequently prepared and analysed the first product of the action of chlorine on styrole. The analyses proved however to us that only on one occasion were we fortunate enough to have hit the proper moment when the action of chlorine must be interrupted. All the other combustions, which we pass over, gave a constantly varying, but always too small a proportion of carbon.

Burned with chromate of lead the following results were obtained:—

0·3553 grm. of chlorostyrole gave 0·7200 grm. of carbonic acid and 0·1505 of water.

From which the following formula and theoretical numbers are deduced, $C_{16}\ H_8\ Cl_2$.

			Theory.		Experiment.
16	equivts.	Carbon . .	1200	54·91	55·26
8	...	Hydrogen .	100	4·57	4·70
2	...	Chlorine . .	885·3	40·52	
1	...	Chlorostyrole	2185·3	100·	

By heating chlorostyrole it is decomposed into a new oily product with evolution of hydrochloric acid. This product, which is probably $C_{16}\left\{\begin{matrix}H_7\\Cl\end{matrix}\right\}$, is obtained in more considerable quantities when chlorostyrole is distilled with caustic lime. We have not examined it more closely. The formula of styrole derived from nitrostyrole is thus completely supported by the analysis of the bromine and chlorine compounds.

By the continued action of chlorine for several days on styrole in direct sunlight, that oil is changed into a thick viscid fluid, with the evolution of a very large quantity of hydrochloric acid. This substance is not even the last product of the action, as by further continuance hydrochloric acid is still given off.

The same fact is observed on submitting styrole to the action of chlorate of potash and hydrochloric acid.

Action of Heat on Styrole.

Metastyrole.— The remarkable change experienced by styrole under the influence of heat has been already mentioned in the preceding pages. We stated that in rectifying the oil a considerable portion of pure unchanged styrole passed over

at first, but at a certain point the contents of the retort became thick, and on cooling solidified into a firm transparent vitreous mass.

On first observing this phænomenon we thought it arose from the conversion into resin by the action of the air of a portion of the raw oil which had been standing in a bottle only half-filled, and that this substance being held in solution by the remaining fluid oil, was separated on distilling the latter from it. A similar idea seems also to have occurred to Simon, from his bestowing the name of oxide of styrole on the residue found in the retort on submitting styrole to distillation.

We soon convinced ourselves that this idea was erroneous by distilling a second time a portion of newly-rectified oil. A very considerable residue of solid matter, though not quite so great as in the first distillation, was observed to remain in the retort. The same amount was further found in a third, fourth and every succeeding distillation. The rapidity with which styrole changes into the solid substance, indicated sufficiently that it could not be from combination with oxygen. This fact was besides established by direct experiment. Indeed so little attraction has styrole for oxygen, that it can be left exposed to air for weeks together without any change in its colour. A portion of oil was confined for several months over mercury in a tube filled with oxygen gas without the least diminution in the volume of the latter. We soon recognised that this metamorphosis of styrole takes place without loss of or addition to any one of its elements, and solely through a change in the molecular structure of this body produced by the action of heat. Analysis as well as synthesis has equally proved that styrole and the vitreous mass (for which we propose the name of metastyrole) possess the same constitution per cent.

Metastyrole, when prepared from colourless oil, is equally transparent, and possesses the same powers of refraction as the latter body*. On the other hand, it completely loses the characteristic odour and taste which distinguish styrole. Metastyrole is totally inodorous and tasteless. At the ordinary temperature this body is hard and can be cut with a knife. By heat it becomes soft, and can be drawn out into threads, which strikingly resemble spun glass. It is insoluble in water and alcohol, as well in the cold as when heated. In boiling æther a small portion is dissolved, which, on leaving the solution to spontaneous evaporation, becomes attached to the sides

* There is scarcely an organic body which refracts the rays of light so strongly as metastyrole. It is not improbable that it might be applied to several optical purposes.

of the vessel in a thin almost transparent layer, that can be separated from the glass, and presents a most deceptive likeness to the thin membrane lining the shell of an egg. The portion which has not been dissolved in the æther swells to six or seven times its original volume. This mass contains, when dried at the ordinary temperature, a large quantity of æther, which is driven off only by heat. Turpentine oil also dissolves traces of metastyrole; sulphuric acid is in the cold without action, but on the application of heat carbonizes the metastyrole, with evolution of sulphurous acid. The action of nitric acid will be presently mentioned.

To obtain metastyrole completely pure, and in a condition fit for analysis, advantage was taken of its relations to æther. The vitreous mass was boiled in æther till it was completely converted into the swollen gelatinous matter from which the excess of æther was decanted; this contains the unchanged styrole that had remained in the resinous mass; and after heating the residue in a water-bath, to expel the æther, a completely inodorous and tasteless white spongy mass was left behind, which could be easily reduced to powder. This powder was again boiled in alcohol, dried, and burned with chromate of lead.

0·2955 grm. gave 0·9970 grm. of carbonic acid and 0·2130 grm. of water. Corresponding per cent. to—

Carbon	92·05
Hydrogen	8·00

Styrole contains—

Carbon	92·30
Hydrogen	7·70

This combustion is sufficiently decisive, but to remove all doubt the following experiment was made.

A portion of styrole was confined in a strong glass tube, hermetically sealed by the blowpipe lamp, and placed in an oil-bath, whose temperature was not allowed to rise above 200° C. At the end of half an hour *the styrole had completely changed into metastyrole.* The same result was obtained by sealing a portion of it in small glass bulbs, in which scarcely a trace of air was left, and submitting them to the temperature of boiling water. On the second day the styrole had become thick, and on the third solid.

A bulb of the same size was exposed to the heat of the sun in the hot summer months. The same transformation likewise took place; but at this temperature it required three weeks to produce the same effect as takes place almost imme-

diately at that of 200° C. Intensity and duration * of action are seen here, as everywhere else in nature, to be equivalent.

Light appears, however, to play a part in the transformation of styrole; at least a small portion sent to Professor Liebig five years ago by E. Simon, and which had been kept in a dark press, is still as fluid as if newly distilled.

This metamorphosis of styrole by heat is so much the more extraordinary, as this agent generally acts in a contrary direction, either to liquify or volatilize. The white of egg alone, in certain points, offers some analogy; and these two bodies, at a higher temperature, exhibit likewise, though in a distant degree, the same behaviour.

L. Gmelin † has shown that the coagulated white of egg, heated in a Papin's digester with water to 200° C., becomes again fluid, and forms with the water a yellow liquid. This observation has been lately confirmed by Wöhler and Vögel ‡.

If metastyrole is heated in a small retort over a spirit-lamp, it becomes again fluid, and a colourless oil distils over, which is pure styrole. By a carefully conducted distillation there remains scarcely any residue in the retort.

It was possible that the oil obtained by distilling metastyrole might be another body of the same composition as styrole and metastyrole, but possessing different properties. The regenerated oil forms instantaneously with bromine the characteristic smelling bromine compound. Besides this reaction, which, as will be seen immediately, is not decisive, the action of heat on the regenerated oil is quite conclusive. Heated to 200° C., in a tube hermetically sealed, it is converted into metastyrole, which by a higher temperature is again in its turn reconverted into styrole.

After having ascertained that styrole and metastyrole had the same composition per cent., and that the difference in their physical properties could only arise from a dissimilar arrangement of their molecules, it was of some interest to obtain an explanation of this arrangement. As the specific weight of the vapours of both bodies could not be compared with each other, there remained no other resource but to study more closely the products of decomposition of metastyrole. As bromine and chlorine act only very slowly on metastyrole, sulphuric acid carbonizes it, and by fusing with potash a sim-

* The varying amount of styrole obtained from the different sorts of storax is probably owing to the same metamorphosis produced in the course of time.

† *Handbuch*, 3te Ausgabe, Bd. ii. S. 1053.

‡ *Ann. der Chem. und Pharm.*, Bd. xli. S. 238.

ple conversion into styrole follows; nitric acid was selected as the decomposing agent.

Action of Nitric Acid on Metastyrole.

Nitrometastyrole.—Common nitric acid, either warm or cold, attacks metastyrole but little. Even strong fuming nitric acid acts but feebly in the cold, but on the application of heat dissolves it quickly with the evolution of red fumes. If a sufficient quantity of nitric acid has not been employed, the new product is precipitated on cooling in the form of a slimy substance. On the other hand, if the acid has been in excess, the fluid remains quite clear, from which, on the addition of water, a white curdy mass, which sometimes has a shade of yellow, is precipitated. This is washed with water to remove all trace of nitric acid, and afterwards boiled in alcohol to get rid of any trace of benzoic acid which may have been formed from styrole still remaining in the pores of the metastyrole.

The body thus obtained, and for which we propose the name of nitrometastyrole, is when dry in the form of a white or yellowish, completely amorphous powder, insoluble in æther, alcohol and water, but soluble in fuming nitric and in sulphuric acid. By the application of a gentle heat it burns with a slight deflagration, like many bodies which possess the elements of hyponitric acid, and with a strong odour of oil of bitter almonds. As the physical properties of this body do not indicate any certainty of its purity, it was burnt to ascertain this point as nearly as possible. After some analyses it was recognised that the new product of decomposition retained traces of undecomposed metastyrole, from the nitric acid solution becoming very turbid on cooling. This fact was proved by dissolving the substance in concentrated sulphuric acid, when the undecomposed metastyrole remains undissolved. On the other hand, by boiling the solution of metastyrole too long in the nitric acid, a mixture was obtained, on precipitating with water, consisting for the most part of nitrometastyrole, and of a second product containing less carbon and more nitrogen.

Nitrometastyrole is obtained pure by dissolving metastyrole in a quantity of acid sufficient to hold it in solution on cooling. Nitric acid must be added to the hot solution as long as it is observed to become turbid on pouring a few drops out into a watch-glass.

The analysis of the substance prepared in this way gave the following results:—

I. 0·3235 grm. of nitrometastyrole gave 0·7230 grm. of carbonic acid and 0·1325 grm. of water.

II. 0·2830 grm. of substance gave 0·6535 grm. of carbonic acid and 0·1330 grm. of water.

III. 0·2865 grm. of substance gave 0·1170 grm. of water.

IV. 0·3142 grm. of substance gave 0·1278 grm. of water.

V. The nitrogen was determined by the method of Dumas, by burning the substance in an atmosphere of carbonic acid, and calculated from its volume.

0·6125 grm. of nitrometastyrole gave 53 cubic centimetres of nitrogen at 329″ barometer and 9° C. thermometer. In per cent.

	I.	II.	III.	IV.	V.
Carbon . .	60·95	61·69			
Hydrogen . .	4·55	5·26	4·53	4·51	
Nitrogen . .					10·06

These numbers correspond to the formula $C_{14} H_6 NO_4$, as is shown by the comparison of the numbers found and calculated.

		Theory.		Mean of experiments.
14 equiv.	Carbon . .	= 1050·00	61·69	61·32
6 ...	Hydrogen .	= 75·00	4·40	4·71
1 ...	Nitrogen . .	= 177·04	10·40	10·06
4 ...	Oxygen . .	= 400·00	23·51	
1 ...	Nitrometastyrole	= 1702·04	100·00	

Taking the most probable supposition, that nitrometastyrole stands in the same relation to metastyrole as nitrostyrole to styrole, or nitrobenzide to benzole, that is, that one equivalent of hydrogen in the carbo-hydrogen is replaced by one equivalent of hyponitric acid, the formula for metastyrole will then be $C_{14} H_7$, from which it is seen, that by the metamorphosis of the body, $C_{16} H_8$, the number of equivalents of carbon and hydrogen in the new compound has diminished by one-eighth.

The formula of nitrometastyrole differs from that of anthranilic acid and protonitrobenzoene by containing one equivalent less of hydrogen. The formula of the two latter bodies is $C_{14} H_7 NO_4$. Late investigations* have shown that protonitrobenzoene, as well as anthranilic acid, when distilled with lime, is decomposed into carbonic acid and aniline. As nitrometastyrole is a body completely analogous to nitrobenzoene, we expected to form under similar circumstances a base with the formula $C_{12} H_6 N$. The experiment did not however turn out to our expectation. On distilling a mixture of lime and nitrometastyrole, a very complicated reaction follows, a large quantity of carbon is deposited, ammonia is evolved, and at

* New Modes of Formation of Aniline, by Dr. J. S. Muspratt and Dr. A. W. Hofmann.—Chemical Memoirs, vol. ii.

the same time a proportionately small quantity of a brown coloured oil passes over. Hydrochloric acid dissolves a large portion of this oil, from which it is again separated by the addition of alkalies. This oil is nothing but *aniline*, which is at once recognised by the dark violet colour it gives with a solution of chloride of lime, and the yellow colour its solution in acids communicates to pine-wood. The formation from nitrometastyrole of this base, which contains more hydrogen than the original substance, is certainly the result of a very complicated reaction, which cannot be exhibited in any equation.

The following is the series of bodies investigated in this memoir:—

Styrole	$C_{16} H_8$
Bromostyrole . . .	$C_{16} H_8 Br_2$
Chlorostyrole . . .	$C_{16} H_8 Cl_2$
Nitrostyrole	$C_{16} \left\{ \begin{matrix} H_7 \\ NO_4 \end{matrix} \right\}$
Hydruret of benzoyl (?)	$C_{14} H_5 O_2, H$
Benzoic acid	$C_{14} H_5 O_3, HO$
Nitrobenzoic acid . .	$C_{14} \left\{ \begin{matrix} H_4 \\ NO_4 \end{matrix} \right\} O_3, HO$
Metastyrole	$C_{14} H_7$
Nitrometastyrole . .	$C_{14} \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right\}$.

The experiments detailed in the preceding pages have proved that the formula of the carbo-hydrogen derived from the storax must be expressed by $C_{16} H_8$. This is, however, likewise the formula of the carbo-hydrogen analogous to benzole, and which is derived from hydrated cinnamic acid by the separation of two equivalents of carbonic acid.

Are Styrole and Cinnamole identical?

This question must necessarily present itself when we consider that storax contains large quantities of cinnamic acid, and that this balsam, according to the views of later celebrated pharmacologists (as Th. W. Martius*), is obtained not by incision but by a kind of distillation.

How easily in this operation a portion of the cinnamic acid might be converted in cinnamole and carbonic acid, we know from the fact of benzoic acid, when passed in vapour through a red-hot tube, being decomposed with ease into carbonic acid and benzole.

The details given us by different chemists on cinnamole

* *Grundriss der Pharmakognosie des Pflanzenreichs*, S. 346.

differ exceedingly from each other. Simon and Marchand prepared this substance by distilling cinnamic acid and caustic lime. Herzog* followed the same course; he obtained a yellowish fluid, which on rectifying gave a light colourless oil, whilst a yellowish-brown, heavy liquid remained in the retort. Cinnamole (named by Marchand and Simon cinnamomine) which has been prepared in this way boils at 89° C. and has a specific gravity of 0·88.

According to Mitscherlich† no product can be obtained in this way possessing a constant boiling-point. He considers the liquid which distils over on rectification as a mixture of different carbo-hydrogens of similar composition, and suspects that it contains benzole.

Finally, Gerhardt and Cahours‡ have stated that a mixture of 1 part cinnamic acid and 4 parts baryta, when distilled, gave a product having a constant boiling-point.

The formula $C_{16} H_8$ was controlled by a determination of the specific gravity of the vapour, and by the analysis of a bromine compound.

The properties described by the last two chemists as belonging to cinnamole (cinnamene), correspond completely with those of styrole. Cinnamole boils, according to Gerhardt and Cahours, at 140° C. It forms with chlorine a fluid, and with bromine a crystalline compound, the latter having the formula $C_{16} H_8 Br_2$. With nitric acid it gives rise to a product which appears to be benzoic acid. In one point, however, they differ. Cinnamole does not possess the property of forming by heat an isomeric solid compound. Gerhardt and Cahours do not mention in their memoir anything of this phænomenon, which, if it existed, could not have escaped their observation in the determination of the specific gravity of the vapour. This determination could not in reality have been made at the temperature mentioned. Styrole was exposed for three or four hours in an oil-bath to a temperature of 182° C. (the same temperature by which Gerhardt and Cahours made the determination of the specific gravity of the vapour), without, however, being altogether volatilized. There remained constantly a considerable portion of metastyrole behind.

To obtain accurate results on this point, we prepared cinnamole by means of lime and baryta. With respect to the action of the lime, we obtained the same results as Mitscherlich. The distilled product is a mixture of different bodies.

* *Arch. der Pharm.*, 2 Reihe, Bd. xx. S. 167.

† *Monatsbericht der Ber. Acad. u. Lerb.* 4 Auf. Bd. i. S. 179.

‡ *Ann. de Chim. et de Phys.*, 3rd ser. t. i. p. 60, and *Ann. der Chem. u. Pharm.* Bd. xxxviii. S. 96.

His suspicion of the presence of benzole we found to be also correct. The body described by Herzog under the name of cinnamole was evidently benzole mixed with traces of other materials. The boiling-point and specific gravity given by him are in themselves sufficient evidence. By distilling a considerable portion of cinnamic acid with lime we easily obtained proof of this identity in the following manner:—The rectified product was submitted again to an interrupted distillation. The oil which passes over under 100° C. was collected by itself, and after treatment with fuming nitric acid, was then exposed to the action of a reducing agent. Aniline was thus obtained, which is easily recognised by its characteristic properties.

It was probable that the portion of fluid which boils at a higher temperature contained cinnamole. We endeavoured by interrupted distillations to separate it, but could not obtain any liquid having a constant boiling-point. The thermometer rose at last above 200°. The portion distilled at 140° formed with bromine a white crystalline mass, which in appearance and smell possessed the most striking similarity to bromostyrole. This crystalline compound was probably *bromocinnamole*, as no styrole could be supposed to exist in it, no trace of residue being left in repeated distillations.

Cinnamole obtained, according to Gerhardt and Cahours' plan, by distilling cinnamic acid with baryta, proved, after rectification, a colourless fluid, which in point of smell was very similar to styrole, though the former was rather more agreeable than the latter. With bromine it forms a crystalline compound having very much the appearance of bromostyrole. Unfortunately a sufficient quantity was not obtained to determine the boiling-point.

As a further point of comparison, a portion of the product (prepared from lime and cinnamic acid), distilled at 140°, was sealed up in a strong tube. Another tube was filled with the oil made according to the plan of Gerhardt and Cahours, and several others with styrole. All these tubes were placed in an oil-bath heated to 200° C. After half an hour the bath was allowed to cool and the tubes removed, when the styrole was found to have become solid, whilst the substances prepared from cinnamic acid by lime and baryta had lost nothing of their fluidity.

This experiment appears at first sight to negative the idea of the identity of the two substances. When, however, it is considered that the product obtained on distilling cinnamic acid and lime contains other bodies besides cinnamole, and that the substance prepared from baryta and the same acid

was in too small a quantity to be more closely investigated, it is evident that the solution of this question must be reserved for future investigations.

Should these prove in an unequivocal way the difference of the two bodies, it would be of great interest to ascertain from what material styrole has its origin. For this purpose it would be in the first place particularly important to gain some information about the source from which *Styrax liquidus* is obtained. The only authentic information we possess on this point is given by Martius*, namely, that it is introduced through Suez and Trieste, is named by the East Indians *Cotter Mija*, and is produced from a tree called *Rosa Mallas*. From this tree two products are, according to Martius, obtained, the one, the common *Styrax liquidus*, through a sort of distillation; the other a balsam, which is very rarely to be met with in commerce. An investigation of the latter would be of great interest.

Postscript.

The preceding memoir was finished in its principal points when the investigation of the products of distillation of dragon's blood by Glenard and Boudault† appeared.

A short notice of this subject had been earlier laid before the French Academy‡. What was then stated, however, did not lead us to suspect in the slightest degree that the products obtained by distillation from dragon's blood could stand in any relation to our investigation of fluid storax. Their late memoir, which contains many essential corrections of the former communication, showed us at first sight the connection between it and our investigation. Messrs. Glenard and Boudault having communicated some striking results, not easily to be understood, it appears to us not to be without interest to conclude this memoir with a few remarks on the investigation of the French chemists, as our experiments furnish a key to their difficulties.

Glenard and Boudault, by distilling dragon's blood, obtained, in addition to water and some acetone and benzoic acid, a reddish-brown oily fluid, which is a mixture of different bodies. From this they isolated two carbo-hydrogens, which they named dracyl and draconyl.

For their preparation the raw oil was submitted anew to distillation, and the product, distilled at 180° C., was collected by itself; it contains dracyl and draconyl. To separate them,

* *Briefliche Mittheilung.*

† *Journ. de Pharm. et de Chem.* 3me ser. t. vi. p. 250.

‡ Ibid. t. i p. 274, and *Ann. der Chem. u. Pharm.* Bd. xlviii. S. 343.

the mixture must be several times distilled at a low temperature, never reaching the boiling-point. What passes over is a colourless fluid, and consists of dracyl, with a small quantity of draconyl; the solid residue in the retort is entirely draconyl.

To free the dracyl from the draconyl, "*which passes over dissolved in the vapour of the former*," it must, acccording to Glenard and Boudault, be several times distilled over hydrate of potash. The potash appears here to form no combination with the draconyl, "*but only to modify it in such a way that it is no longer soluble in dracyl.*" The draconyl remaining in the retort is to be washed with alcohol to remove the dracyl and then heated to 150° C., by which the last traces of dracyl are driven off.

Pure draconyl is, according to these chemists, a colourless mass of a shining appearance; insoluble in water, alcohol, æther and potash-ley, but soluble by heat in fat and æthereal oils.

Draconyl is not volatile, but by aid of another carbo-hydrogen it can be distilled. (Il n'est point volatile; toutefois, il peut distiller à la faveur d'un autre hydrogène carboné).

From the analysis of Glenard and Boudault, draconyl contains two equivalents of carbon to one of hydrogen. The formula found for the substance obtained by the action of nitric acid on draconyl, and for which they proposed the name nitrodraconyl, was $C_{14}\,H_6\,NO_4$. This gives for draconyl $C_{14}\,H_7$. That substance sealed up in a tube and heated to a high temperature is converted into a yellow fluid, which boils at 140° C., and has the same composition as draconyl itself. Thus far are the details given by Glenard and Boudault. On comparing the results of these chemists with ours, it is at once seen that *metastyrole and draconyl are identical.* A satisfactory explanation is immediately found for some things in their memoir otherwise incomprehensible. We cannot, for instance, understand how a body with the properties given it, and totally devoid of volatility, can distil by the aid of another carbo-hydrogen. In boracic acid, indeed, we possess a body in itself completely fixed, but which volatilizes in not inconsiderable quantities with the vapour of boiling water; still this quantity is but a trace in comparison with the amount of the watery vapour. Our experiments however explain quite easily this difficulty. *Draconyl (metastyrole) exists in the corresponding product of the distillation of dragon's blood, not as such, but in the form of styrole.* After the distillation only is this styrole changed into metastyrole (draconyl). It is not easily understood why the mixture must be repeatedly distilled to obtain draconyl,

and why the distilled dracyl obstinately retains a small portion of draconyl (that is, in this case styrole), which can only be removed by continued heating with hydrate of potash. The hydrate of potash is here really unessential, the separation being produced by the action of the heat alone. The most certain and complete mode of separation would be to seal up the mixture in a strong tube of glass, and heat it for an hour at 200° C. in an oil-bath. On opening the tube, the dracyl could be directly distilled from the metastyrole (draconyl).

Although, on making a comparison of the two bodies, there can be no doubt of their identity, it appeared desirable to substantiate the assertion by direct experiment. The point would be settled could there be obtained from dragon's blood styrole or any of its compounds. We are indebted to Dr. J. S. Muspratt for a quantity of the oil collected at 180° C. in the rectification of the raw product. On submitting this to a new distillation, dracyl alone at first passes over, then a mixture of dracyl and styrole, and finally almost pure styrole shortly before the metastyrole (draconyl) is formed in the retort. With bromine it forms a crystalline body, possessing all the properties of bromostyrole. Much weight however was not to be attached to this reaction, as it was found that dracyl also formed with bromine a compound which crystallized in beautiful needles. To decide the point, a quantity of the fluid was sealed in a strong tube and heated in an oil-bath to 200° C. On withdrawing it at the end of an hour, the contents were not quite solid, but the original light, moveable fluid was converted into a jelly of tenacious consistency, which, on allowing the tube to cool, could scarcely be moved. The styrole had evidently contained a small quantity of dracyl.

The appearance of styrole in the products of distillation of storax and dragon's blood brings these two substances into close relation with each other; probably they both contain the same, or a similar principle, which by distillation is decomposed in a similar manner. Its isolation would be of great interest. For this purpose however the analysis of the resins must be conducted in a different manner than has hitherto been the case. Cinnamic acid has not as yet been observed in dragon's blood.

CXXXIX. *Note on the useful applications of the Refuse-Lime of Gas-works.* *By* Thomas Graham, *Esq.*, *F.R.S.*

I HAD lately occasion to examine the lime as removed from a dry lime purifier. The gas before reaching the latter had been washed with dilute sulphuric acid, which accounts

for the absence of ammonia and cyanogen compounds. The lime had not been exposed more than a few hours to the air before it was operated upon. Still, to my surprise, it did not blacken an acid salt of lead, and contained no sulphuret of calcium. It was not dried, but analysed in a damp state, exactly as it is sent out of the works to be used as manure.

Composition of Gas-Lime.

Hyposulphite of lime . . .	12·30
Sulphite of lime	14·57
Sulphate of lime	2·80
Carbonate of lime	14·48
Hydrate of lime	17·72
Sulphur	5·14
Sand	·71
Water combined	8·49
Water (free)	23·79
	100·

With no more than a trace of ammonia and cyanogen.

The lime in the porous condition in which it is taken from the dry-lime purifiers, absorbs oxygen so rapidly from the air as to heat, and hence the state of oxidation in which the sulphur is found. If the lime be very damp, or diffused through a quantity of water, as it comes from the wet-lime purifiers, then the absorption of oxygen is much slower. The fluid portion then contains in solution the bisulphuret of calcium of Herschel, which may be crystallized from it; and at first very little else.

After the first rapid absorption of oxygen, the further oxidation of the gas-lime is decidedly slow. A specimen kept in an open vessel, and repeatedly moistened and rubbed to powder when it dried, was found after three months' exposure to retain 7 per cent. of sulphurous acid, besides all the free sulphur originally present. The hyposulphurous acid had entirely disappeared. Hence, if added to soil as manure, gas-lime must be powerfully deoxidizing, a property which will generally impair its utility.

It appears advisable, where the refuse-lime does not possess any value from ammonia, to dry it strongly, or roast it. It would thereafter consist of nearly equal weights of sulphate and carbonate of lime, and be in the condition most valuable as a manure.

Refuse-lime, such as was examined, may be recommended as a convenient and most œconomical source of the hyposulphites. The lime, after being taken from the purifiers, should be exposed to air for two or three days, till it loses all smell

of sulphuretted hydrogen. The highly soluble hyposulphite of lime may then be dissolved out by little more than an equal weight of cold water. The solution may be evaporated at 120°, and the hyposulphite of lime crystallized out; or, the solution, by adding carbonate of soda, converted into hyposulphite of soda, which is a more stable salt, may be evaporated at a higher temperature, and crystallizes more easily.

From the refuse-lime, one-sixth of its weight of crystallized hyposulphite of lime has been obtained in a state of purity by a single crystallization. When the gas is washed with sulphuric acid to remove ammonia, before being conducted into the lime-purifier, it yields the refuse-lime more suitable for this purpose. The preparation of the hyposulphites in quantity is becoming the more important, as besides their use in electro-plating and photography, they are likely to be applied largely to the extraction of chloride and bromide of silver from silver ores.

CXL. *Contributions to the Knowledge of Conjugate Compounds.* *By* Dr. H. Kolbe, *Chemical Assistant in the University of Marburg.*

THE examination of the products arising from the decomposition of sulphuret of carbon by means of chlorine has led to the discovery of an interesting series of bodies, which belong, almost without exception, to the class of the so-called conjugate compounds*, and among them the substitution of chlorine by hydrogen is particularly observed, which will probably throw considerable light on the constitution of certain organic combinations. These compounds, produced almost by the direct combination of their elements, have such a strong similarity to those considered to belong to organic chemistry, that it is impossible here to draw a distinct line between organic and inorganic bodies.

I have already† shown that chlorine and sulphuret of carbon carefully dried are decomposed into a mixture of chloride of sulphur and perchloride of carbon; this takes place not merely at a red heat but at ordinary temperatures, in daylight as well as in the dark. This perchloride of carbon is identical with Regnault's "*ether chlorhydrique de l'esprit de bois perchlorure*," and may be obtained with ease from the chloride of carbon. Perchloride of carbon does not enter into direct combinations, but it unites with sulphurous acid when both are in a nascent state, and forms conjugate, neutral, indifferent bodies, which Berzelius and Marcet discovered when they

* "Corps copulés" of Gerhardt.

† Liebig's *Annal.* Bd. xlv. p. 41.

digested sulphuret of carbon with moistened chlorine or nitric acid*. I call this white, volatile, crystallized compound sulphite of perchloride of carbon, $C\,Cl_2\,SO_2$. It may be obtained in large quantities by digesting peroxide of manganese and hydrochloric acid for several days in a close vessel with sulphuret of carbon, and after the decomposition is complete distilling the mixture. Its formation is explained by the following formula,—

$$\left.\begin{matrix} C\,S_2 \\ 4Cl \end{matrix}\right\} \begin{matrix} C\,Cl_2 \\ 2S\,Cl \end{matrix} + 2HO = \left\{\begin{matrix} C\,Cl_2\,SO_2 \\ 2H\,Cl \\ S. \end{matrix}\right.$$

Sulphite of perchloride of carbon suspended in water is reduced by chloride of tin, sulphuretted hydrogen, or sulphurous acid, and converted with the loss of one equivalent of chlorine into sulphite of chloride of carbon, $C\,Cl\,SO_2$, a colourless, inodorous, and very unstable combination, soluble in water and alcohol. The solution in water is decomposed upon exposure to the air, combining with one equivalent of oxygen, forming oxide of chloride of carbon and sulphurous acid. Chlorine occasions a precipitate of regenerated sulphite of perchloride of carbon. Bromine also produces a similar insoluble combination, which will be the subject of a future examination. Iodine occasions no precipitate. The behaviour of sulphite of perchloride of carbon towards the caustic alkalies gives rise to a series of conjugate hyposulphates, which have the greatest similarity to one another, although their conjunctives, by which they are alone distinguished, are bodies of quite a different chemical nature. The acids thus produced do not show the slightest similarity to sulphurous acid; the chemical properties of the latter are upon formation of the conjoined bodies completely changed, and they have obtained properties and a power of combination which place them by the side of the strongest inorganic acids. The first of these combinations is hyposulphate of chloride of carbon, $HO + C_2\,Cl_3, S_2\,O_5$. It contains as a conjunct perchloride of carbon, and is formed together with chloride of potassium when the sulphite of perchloride of carbon is dissolved in caustic potash. The potash salt crystallizes after evaporation of the neutral solution in large rhombic tables, which effloresce upon exposure to the air. The crystals contain one atom of water; the effloresced salt is free from water, and is composed of $KO + C_2\,Cl_3, S_2\,O_5$. This decomposition is thus explained—

$$\left.\begin{matrix} 2C\,Cl_2\,SO_2 \\ 2KO \end{matrix}\right\} \begin{matrix} KO + C_2\,Cl_3, S_2\,O_5 \\ K\,Cl. \end{matrix}$$

* Berzelius's Chemistry, i. p. 622.

The hydrous hyposulphate of chloride of carbon, which is obtained by precipitation of the baryta salt with sulphuric acid, crystallizes upon evaporation in small prisms, not permanent in the air, which may be heated to 150° without decomposition. They are not oxidated by boiling with nitric, nitromuriatic or chromic acids; nitric and hydrochloric acid may be distilled off from it without any change. The salts of hyposulphate of chloride of carbon are soluble in water and in alcohol, and easily crystallizable. They are decomposed by heat into sulphurous acid, chloro-carbonic oxide gas, and the metallic chloride, which last remains free from sulphuric acid, and is colourless. The barytic salt is formed like the alkaline salt, by solution of the sulphurous perchloride of carbon in baryta water; it crystallizes upon evaporation in large four-sided tables; at 100° Cent. it is composed of $BaO + C_2 Cl_3, S_2 O_5 + aq$. The remaining salts are formed by neutralising the free acid with a basic carbonate. The ammoniacal salt crystallizes most readily in fine large prisms.

Hyposulphate of chloride of formyl, $HO + C_2 HCl_2, S_2 O_5$, is the second in this class of coupled acids. It is formed by the substitution of one equivalent of hydrogen for one equivalent of chlorine of the hyposulphate of chloride of carbon, when zinc is dissolved by hyposulphate of chloride of carbon, which takes place without the evolution of hydrogen, but with the formation of hydrochloric acid,

$$\left.\begin{matrix} HO + C_2 Cl_3, S_2 O_5 \\ 2Zn \end{matrix}\right\} \begin{matrix} ZnO + C_2 HCl_2, S_2 O_5 \\ Zn\,Cl. \end{matrix}$$

The potash salt, $KO + C_2 HCl_2, S_2 O_5$, is also obtained by boiling caustic potash with sulphite of chloride of carbon, which combines with one atom of water,

$$\left.\begin{matrix} 2C\,Cl\,SO_2 \\ KO \\ HO \end{matrix}\right\} KO + C_2, HCl_2, S_2 O_5.$$

This salt is easily soluble in water and hot alcohol, difficultly soluble in cold alcohol; crystallizes from a hot, saturated alcoholic solution in small, shining nacreous leaves; dried at 100° it is anhydrous, and is resolved at 250° C. into hydrochloric acid, sulphurous acid, carbonic acid and oxide of carbon; chloride of potassium slightly coloured by charcoal remains behind. The free acid may be obtained by precipitating the alcoholic solution of the potash salt with sulphuric acid. The filtered acid solution may be evaporated, and the excess of sulphuric acid precipitated either by carbonate of lead or baryta water. The hydrate of the hyposulphate of chloride of formyle forms a thick liquid, which crystallizes,

in vacuo over sulphuric acid, in small scales, and is similar both in its stability and power of combination to the hyposulphate of chloride of carbon. The silver salt, $AgO + C_2HCl_2, S_2O_5$, is very sensitive both to light and heat; it can only be obtained in a crystallized state in a vacuum and in the dark; when dry it will bear a temperature of 100° C. without change.

Hyposulphate of chlor-elayl, $HO + 2C_2H_2Cl, S_2O_5$, contains chloride of elayl as a conjunct, or another isomeric compound. It is formed by the substitution of two equivalents of hydrogen for two equivalents of chlorine of the hyposulphate of chloride of carbon, when a solution of hyposulphate of chloride of carbon and potash is acidified by sulphuric acid, and decomposed by a galvanic current. Two pairs of the Bunsen carbon and zinc series are required for it; two amalgamated zinc plates were the electrodes.

The average power of the current, as measured by Weber's galvanometer, was 82°, equal to a deflection of the needle of 55°. The hydrogen in the nascent state unites with the chlorine of the hyposulphate of chloride of carbon at the cathode, and forms muriatic acid; the equivalents of chlorine are substituted by equivalents of hydrogen. This exchange only proceeds in the formation of the hyposulphate of chlor-elayl, as long as the fluid which is to be decomposed contains an excess of acid,

$$\left.\begin{matrix} KO \\ 4HO \end{matrix}\right\} + C_2Cl_3S_2O_5 \left\{\begin{matrix} KO + C_2H_2Cl, S_2O_5 \\ 2HCl \\ 2O. \end{matrix}\right.$$

The oxygen is not set free by the above decomposition, but unites with the zinc of the anode; but if the fluid is so far saturated with sulphate of zinc, that the reduced zinc is deposited on the cathode, then it must be precipitated with carbonate of potash, and the filtered fluid being again rendered acid, must be once more exposed to decomposition by the current. This operation is to be repeated as long as traces of chlorohyposulphate of formyl are perceived, which will be known when the potash salt of the hyposulphate of chlor-elayl, to be extracted out of the fluid precipitated by carbonate of potash and evaporated to dryness, gives out muriatic acid at a red heat. It is impossible to separate both the salts when they appear mixed.

The potash salt of the hyposulphate of chlor-elayl is very much like the salt of hyposulphate of chloro-formyl; it crystallizes out of hot alcohol in small needles, and differs, as before stated, principally by its behaviour at a red heat. It

is precipitated by diluted sulphuric acid and chloride of calcium, which remains of a dark black by the separation of carbon; in fine, the hyposulphate of chlor-elayl is quite like the hyposulphate of chloro-formyl. If a platinum anode be used in the above decomposition of the potash-hyposulphate of chloride of carbon, then the free oxygen acts on the compound and oxidizes it. There goes off at the anode a mixture of chlorine, oxygen and carbonic acid, and after the decomposition is finished there is contained in the fluid only hypochlorate of potash and bisulphate of potash. Under the same conditions the solution of chloride of potassium changes into hypochlorite of potash, and ultimately into chlorate of potash; hypochlorite of potash is only formed in the presence of free acid. Iodide of potassium likewise becomes iodate of potash; I could not produce a *fluorate* of potash from the decomposition of fluoride of potassium.

Hyposulphate of methyl = $HO + C_2 H_3, S_2 O_5$. This compound concludes the series of conjugate hyposulphites. It contains as conjoined a carbo-hydrogen corresponding to the bichloride of carbon, which possesses the same composition as the radical of methyl. It may be produced in the same manner as the above acid, by means of the galvanic current, from hyposulphate of chloride of carbon and potash when the solution contains free alkali. The decomposition takes place as represented by the following formula:—

$$\left.\begin{matrix} KO \\ 6HO \end{matrix}\right\} + C_2 Cl_3, S_2 O_5 \left\{\begin{matrix} KO + C_2 H_3 \\ 3H\,Cl \\ 6O \end{matrix}\right. = S_2 O_5.$$

The uncombined hyposulphate of methyl exhibits also the greatest resemblance to the hyposulphate of chloro-formyl, and is produced like it from the alcoholic solution of the potash salt by precipitating with sulphuric acid. The concentrated acid crystallizes *in vacuo* over sulphuric acid in delicate, easily soluble laminæ, which may be heated to 130° C. without decomposition. It cannot be oxidized by nitric or by chromic acid, and forms only insoluble crystalline salts.

The potash salt, $KO + C_2 H_3, S_2 O_5$, at 100° C. is dissolved with difficulty in cold absolute alcohol; and the hot saturated solution crystallizes during the cooling in soft, silky fibres, which form so close a texture, that the mother-water appears gelatinous. On being heated a liquor separates, which has a neutral reaction, and there is also obtained a fetid, volatile product, not further examined: there remains bisulphate of potash mixed with charcoal.

The lead salt, $PbO + C_2 H_3, S_2 O_5 + Aq$, crystallizes by

spontaneous evaporation in large prisms: it has a feeble acid reaction, a sweetish taste, and when dried at 100° C. is anhydrous. By boiling with oxide of lead a basic salt is produced, $PbO + C_2 H_3 S_2 O_5 + 2PbO$, which becomes dull by exposure to the air from the separation of carbonate of lead, and in a vacuum dries up into an amorphous saline mass.

The silver salt, $AgO + C_2 H_3, S_2 O_5$, admits of evaporation by heat, and only becomes slowly blackened by exposure to the light. It crystallizes in small, thin, anhydrous laminæ, and by a red heat leaves pure metallic silver. All the four conjugate hyposulphates agree further in not uniting with oxide of ethyl to form an æther. In respect to its composition, the hyposulphate of chloro-carbon is ranked with the oxalate of chloro-carbon, or the combination which is known under the name of chlor-acetic acid.

Oxalate of chloro-carbon, $HO + C_2 Cl_3 C_2 O_3$.—As respects the chemical properties of this compound, I have but little to add to the minute investigations of Dumas, as I found that Melsen's statement on the reproduction of acetic acid by means of the potassium amalgam was perfectly corroborated. Respecting its formation, I may mention that it can be also obtained from the oxidation of chloral by fuming nitric acid, or with a mixture of chlorate of potash and muriatic acid,—

$$C_4 Cl_3 HO_2 + O_2 = HO + C_2 Cl_3 C_2 O_3.$$

Further, chloral is to oxalate of chloro-carbon what aldehyde is to acetic acid. This body, about the constitution of which there have already been so many opinions expressed, is also to be considered as a conjoined compound of formylic acid with perchloride of carbon, $C_2 Cl_3 O_2 HO_2$, an opinion which not only shows the oxidation to form oxalate of chloro-carbon, but also explains simply and sufficiently the origin of aldehyde and the known decomposition into perchloride of formyl and formic acid.

Perchloride of carbon and oxalic acid can unite to form oxalate of chloro-carbon, if they are brought together at the moment of their production. This takes place if chloride of carbon (C Cl) is exposed, under a layer of water, with chlorine to the sunlight. One part of the perchloride of carbon produced is decomposed in the nascent state by water to form muriatic acid and oxalic acid; the latter of which unites with another part of the perchloride of carbon, thus—

$$\left.\begin{matrix} 2C_2 Cl_3 \\ 4HO \end{matrix}\right\} HO + C\,2\,Cl\,3C_2 O_3$$
$$3H\,Cl$$

The oxalate of chloro-carbon remains dissolved in water, and may be ultimately separated from the muriatic acid mixed

with it and crystallized, by evaporation *in vacuo* over lime and sulphuric acid. The silver salt of this acid does not contain any hydrogen: it detonates by heating, and becomes black by exposure in the air. 0·396 grm. left by a red heat 0·210 grm. chloride of silver.

0·658 grm. burned with oxide of copper, produced 0·214 grm. of carbonic acid. These numbers correspond in 100 parts to 39·9 of silver and 8·9 of carbon. The formula $AgO + C_2Cl_3C_2O_3$ requires 40·0 silver and 8·9 of carbon.

If we admit these simple facts, then it follows that the acetic acid, which has been until now only known as a product of the oxidation of organic matters, can be also formed synthetically from its elements. Sulphuret of carbon, chloride of carbon, and oxalate of chloro-carbon are the members which in conjunction with the elements of water constitute the means of transition from carbon to acetic acid.

The oxalate of chloro-carbon can also be changed like the hyposulphate of chloro-carbon by the galvanic current, alkali being present, into acetic acid. I have likewise obtained certain signs of the existence of the corresponding members of the hyposulphate of chloro-formyl and hyposulphate of chlor-elayl, which lie between the oxalate of chloro-carbon and acetic acid. All these facts seem to speak in its favour, and make it at the same time highly probable that the acetic acid is a conjoined compound, or, in other words, methyl-oxalic acid, $HO + C_2H_3, C_2O_3$.

I shall communicate these observations in a future paper after the examination is terminated.

It follows from the above, that without doing homage to the new theory of substitution, we may assume, as an undoubted fact, a reciprocal exchange of hydrogen and chlorine. Methyl or perchloride of carbon may be conjoined with hyposulphuric acid, the character of the compound will be little changed by it; but nevertheless, there is no reason for supposing hyposulphate of methyl to be hyposulphate of chloro-carbon, in which hydrogen takes the part of chlorine. The assertion reversed would be equally true. It is a constant fact that several, perhaps, isomorphic combinations *can* be represented as conjuncts of one and the same acid, without an essential change of the acid properties of the conjoined body. The organic bases containing chlorine, which have been newly discovered by Hofmann, may perhaps be elucidated in a similar point of view.

CXLI. *On Toluidine, a new Organic Base.* By James Sheridan Muspratt, *Ph.D.*, *and* Augustus William Hofmann, *Ph.D.*

THE artificial formation of different compounds hitherto considered as exclusively the products of the vital process has been during the last ten years among the most interesting results furnished by the study of the metamorphoses of organic bodies. We have found in *cyanic acid* and *ammonia* the compounds by whose union *urea* is produced; by the oxidation of *uric acid* with pure oxide of lead *allantoin* formed, a crystallizable matter existing in the allantoic fluid of the cow; and *salicine* and *fousel oil*, when properly treated with substances rich in oxygen, furnish us the acids produced in the process of the vegetation of *Spiræa ulmaria* and *Valeriana officinalis*; and, lastly, the composition and properties of the volatile oil of *Gaultheria procumbens* were only necessary to be known for its artificial production to succeed immediately in the hands of the chemist.

Still the greater part of the researches made during the last ten years in organic chemistry have been of a purely *analytical* nature. Although the metamorphoses of a considerable number of organic bodies have been studied, still this has not been with the view of obtaining certain compounds which suggested themselves to the theoretical inquirer, but rather with the intention of drawing conclusions as to the composition and properties of the body which was the starting-point of the investigation from the properties and nature of the products of its decomposition.

From such inquiries we have reaped a rich harvest of experience, they have made us somewhat better acquainted with the transformations which an organic substance suffers under the influence of the most different agents, and have thus qualified us for attempting the formation of a given compound in one or the other way. But few such *synthetical* experiments have as yet been performed; it is likely that a great number will be made without success, which may be probably owing to suppositions contrary to nature; but it cannot be doubted that we shall proceed in this direction with greater certainty when a number of even unsuccessful trials of this kind has been undertaken.

The artificial production of bodies occurring in nature presents at first a purely theoretical interest, but all will agree that such endeavours may become of the highest practical importance when they consider those compounds which now take a high place in medicine, the arts and commerce. The

valerianic acid is already so often employed in medicine, that its production upon a large scale from fousel oil cannot long be postponed, and this becomes the more feasible, as we can obtain the latter in such large quantities as a secondary product in rectifying distilleries. Of what influence would be the invention of a process for procuring the medicinal vegetable alkaloids in a simple artificial way? If a chemist should succeed in transforming in an easy manner *naphthaline* into *quinine*, we would justly revere him as one of the noblest benefactors of our race.

Such a transformation has not as yet succeeded, but this does in nowise show its impossibility. We have become acquainted in the last ten years with a remarkable series of artificial organic bases, and, with the exception of urea, which in many respects differs from the other organic bases, there is *none* which has been met with in nature, but there are many among them bearing the greatest similarity with the natural ones in properties and composition.

The artificial bases which we now possess have been obtained in very different ways. The first bases procured by Liebig*, *melamine*, *ammeline* and *ammelide*, were produced by the decomposition of sulphocyanide of ammonium in the heat; and others, such as *aniline*† and *chinoline*‡, were formed by fusing alkalies with organic matters, or by distillation only, as the first mentioned and *lophine*, recently discovered by Laurent§. Basic bodies have further been produced by the action of ammonia upon organic compounds. To these belong the *Thiosinnamine* of Will‖, and *amarine* obtained by Laurent** from the hydruret of benzoyl, and another highly remarkable base newly prepared by Fownes†† from the so-called artificial oil of ants. Lastly, chemists have succeeded in replacing the sulphur in sulphuretted compounds by oxygen, and thus obtaining new bodies possessing basic properties. We see examples of this kind in *sinnamine* formed by Varrentrapp and Will from the *thiosinnamine*; and Simon's *sinapoline*, obtained by the desulphuration of oil of mustard.

These modes, however, for the formation of organic bases are only applicable in a very few cases, as the bodies from which they were derived were themselves more or less insulated and peculiar, and therefore till chemists succeed in dis-

* *Annal. der Chem. und Pharm.*, Bd. x. S. 1.
† Fritzsche, *Annal. der Chem. und Pharm.*, Bd. xxxvi. S. 84.
‡ Gerhardt, *Annal. der Chem. und Pharm.*, Bd. xlii. S. 310.
§ *Compt. Rend.* t. xviii. p. 1016.
‖ *Annal. der Chem. und Pharm.*, Bd. lii p. 8.
** *Compt. Rend.*, t. xix. p. 353.
†† Phil. Trans., 1845.

covering more compounds of the same classes, the formation of basic bodies in this manner must be limited.

It is quite different with another method, by which chemists have also succeeded of late years in procuring basic bodies. Zinin* was the first who conceived the happy idea of investigating the products produced by the action of sulphuret of ammonium upon nitrogenous compounds, which latter were procured by treating various carbo-hydrogens with nitric acid. Zinin investigated in this point of view Laurent's *nitronaphthalase* obtained by the action of nitric acid upon naphthaline, and *nitrobenzide*, discovered by Mitscherlich, and he arrived at the remarkable result that these bodies lose their whole oxygen under the influence of sulphuretted hydrogen, and in assuming hydrogen pass into combinations, presenting in every respect the characters of true organic bases; the two bases formed by Zinin in the manner described, are the *naphthalidam*, for which Berzelius† has lately proposed the more appropriate name of naphtalidine, and *benzidam*, afterwards recognised as identical with aniline. The following comparison of formulæ shows how nearly the original compounds are connected with the required products:—

$$\text{Nitronaphthalase } C_{20}H_7NO_4 = C_{12}\begin{cases} H_7 \\ NO_4 \end{cases}$$

$$\text{Naphtalidine. . } C_{20}H_9N = C_{12}\begin{cases} H_7 \\ Ad \end{cases}$$

$$\text{Nitrobenzide . } C_{12}H_5NO_4 = C_{12}\begin{cases} H_5 \\ NO_4 \end{cases}$$

$$\text{Aniline . . . } C_{12}H_7N = C_{12}\begin{cases} H_5 \\ Ad \end{cases}$$

By this comparison the transformation occurring through sulphuret of ammonium may be considered as ultimately a substitution of the elements of amidogen for those of peroxide of nitrogen, independently of these combinations existing or not in the compounds. Zinin's discovery is very remarkable in its consequences, and will, without doubt, become of vast importance for the group of alkaloids. If we consider how large is the number of carbo-hydrogens already known, all of which change their composition when acted upon by nitric acid, giving compounds corresponding to nitronaphthalase and nitrobenzide; then, supposing these products to suffer also an analogous decomposition with sulphuret of ammonium, there will be no limit to the production of new bases, and we may naturally infer that even those occurring in nature might be

* *Annal. der Chem. und Pharm.*, Bd. xliv. p. 283.

† *Jahresbericht*, xxii. p. 545.

produced if we only succeed in obtaining the appropriate carbo-hydrogen.

A greater correspondence as to properties and chemical character cannot be imagined than that subsisting between aniline and the two following bases: *nicotine* contained in the fresh leaves of the tobacco plant, and *coniine* found by Geiger in all parts of the hemlock (*Conium maculatum*).

According to the analysis of Ortigosa and Belard, lately corrected by Melsens*, nicotine is represented by the formula

$$C_{10} H_7 N,$$

and coniine, by Ortigosa's† formula, which has yet to be confirmed, by

$$C_{16} H_{16} N (?).$$

Now if we could succeed in obtaining the carbo-hydrogens

$$C_{10} H_6$$
$$C_{16} H_{15},$$

there would be no difficulty in procuring, in an artificial way, nicotine and coniine, *i. e.* by treating the product of the action of fuming nitric acid upon the above hydrocarbons with sulphuret of ammonium. We should have—

$C_{10} H_6$ unknown.

$C_{10}\left\{\begin{matrix} H_5 \\ NO_4 \end{matrix}\right\}$ unknown.

$C_{10}\left\{\begin{matrix} H_5 \\ NH_2 \end{matrix}\right\}$ nicotine.

$C_{16} H_{15}$ unknown.

$C_{16}\left\{\begin{matrix} H_{14} \\ NO_4 \end{matrix}\right\}$ unknown.

$C_{16}\left\{\begin{matrix} H_{14} \\ NH_2 \end{matrix}\right\}$ = coniine.

The hypothetical hydro-carbons above cited have not hitherto been obtained; but when we consider how many decompositions yield carbo-hydrogens, and also that the destructive distillation of organic matters promises to furnish us with an inexhaustible supply of these compounds; and as we recognise daily, produced in these processes of transformation, new bodies thoroughly analogous to those looked for, we need not despair of obtaining those sought; and thus, by the destruction of organic compounds, open a new source for the formation of products generated in other ways, and which are produced in the vegetation of plants.

Considerations such as these have led us to undertake

* *Ann. der Chem. und Pharm.*, Bd. xlix. p. 353.
† Ibid. Bd. xlii. p. 313.

a series of investigations concerning the action of sulphuret of ammonium upon various bodies containing, like nitronaphthalase and nitrobenzide, the elements of peroxide of nitrogen.

There occurred in this inquiry some questions the answers to which appeared of interest. Above all, it was necessary to decide whether the transformations suffered by nitronaphthalase and nitrobenzide were identical with those of all similarly constituted bodies. Secondly, it was requisite to ascertain how hydrocarbons behave in which more than one equivalent of hydrogen is replaced by peroxide of nitrogen. Here very different results might be imagined. Lastly, it was of the greatest value to study the properties of those bodies resulting from treating with sulphuret of ammonium the products of the action of nitric acid upon *oxides of hydrocarbons*.

The following is the first of a series of investigations made with regard to the preceding statements. The experiments were performed in the Giessen laboratory, and therefore we cannot refrain from expressing our greatest thankfulness to Professor Liebig for his kind assistance and counsel during the course of them. We commenced by a careful repetition of Zinin's experiments upon the formation of *naphthalidine*, and have procured this body possessing all the properties ascribed to it by that chemist. As to the production of aniline from nitrobenzide, every information has already been given upon that subject*; in fact, we must confirm Zinin's statements in every respect. From among the numerous carbo-hydrogens offering themselves for an investigation we selected two, which, from their particular analogy with benzol, seemed most appropriate for carrying out our object. These are *toluol* and *cumol*. We shall in this treatise communicate the experiments upon toluol.

Preparation of Toluol.

Toluol was some years ago recognised by Deville† among the products of the distillation of Tolu balsam, and this chemist described it under the name benzoéne, which indeed is not happily chosen. Berzelius‡ has given to this body the name *toluine* or toluol, which last we shall retain in our communications. We have proceeded in the preparation of toluol according to the directions of Deville, which we willingly confirm. Eighteen to twenty pounds of the balsam of Tolu

* Vide Hofmann's investigation upon Coal-gas Naphtha, Philosophical Magazine, vol. xxiv. pp. 115, 193, 261.

† *Ann. de Chim. et Phys.* 3 sér. t. iii. p. 168.

‡ *Jahresbericht*, Bd. xxii. p. 354.

were submitted to distillation in glass retorts, partly over an open fire and partly on a sand-bath. There passes over at first aqueous vapour, and when the temperature is sufficiently elevated, a large quantity of benzoic acid (with a slight admixture of cinnamic acid), which solidifies immediately in the recipient into a white crystalline mass. As soon as the fluid distilling over no longer solidified the receiver was changed, and then there condensed a yellow liquid*, which is, according to Deville, a mixture of *toluol* and *benzoic æther*. When it had cooled—a quantity of benzoic acid previously dissolved was deposited—we redistilled and only collected the portions passing over from 130°—140° C. This distillate is deprived of the last traces of benzoic acid by being repeatedly distilled with pieces of solid potash. The fluid obtained in this way possessed nearly all the properties ascribed by Deville to toluol. The product, however, in this manner is extremely small when compared with the quantity of Tolu balsam employed. We have, on account of this, endeavoured to discover another source for getting the toluol in larger quantities, but without success; we therefore deem it necessary to mention this, as it may spare perhaps other vain attempts.

Cahours† has occasionally found in his investigation upon gaultheria oil that the salicylate of the oxide of methyl, when distilled with caustic barytes, furnishes anisol, the same product that the anisic acid isomeric with the former yields under the same circumstances.

$$\underbrace{C_{16}H_8O_6}_{\text{Salicylate of the oxide of methyl.}} + 2BaO = \underbrace{C_{14}H_8O_2}_{\text{Anisol. Dracol.}} + 2(BaO, CO_2).$$

This unexpected transformation seemed to point out a new source for the production of manifold hydrurets of carbon, by treating in a similar manner the various compound æthers.

Anisol differs only from toluol in two equivalents of oxygen.

$$\begin{array}{ll} \text{Anisol} & C_{14}H_8O_2 \\ \text{Toluol} & C_{14}H_8 \end{array}$$

The question now presented itself as to whether toluol could not be produced by the action of caustic barytes or caustic lime upon an æther containing two equivalents less of oxygen than the salicylate of the oxide of methyl? Such an æther is the benzoate of the oxide of methyl:—

* The crystalline mass collected in the first receiver contains likewise a large quantity of the same liquid, which can be separated by mere distillation with water.

† *Ann. de Chim. et de Phys.* 3 sér. t. x. p. 353.

$$\underbrace{C_{16}\,H_8\,O_4}_{\text{Benzoate of the oxide of methyl.}} + 2BaO = \underbrace{C_{14}\,H_8}_{\text{Toluol. Benzoéne.}} + 2(BaO,\,CO_2)?$$

Deville has given benzoate of the oxide of ethyl as one of the products of distillation of Tolu balsam; but if we consider how minute is the difference per cent. between the ethyl and methyl compounds of benzoic acid, as also that Deville did not either analyse the alcohol from the former, or change it into acetic acid, we may readily infer that his compound is not benzoic æther, but benzoate of methyl, which by the temperature acquired in the distillation is partly converted into *toluol* and carbonic acid. Considerations of this kind prompted us to study the action of caustic lime upon benzoate of the oxide of methyl. We passed the vapour of this body over incandescent lime previously strewn in a combustion tube, and obtained an oil which was not dissolved by potash ley. From its comportment and analysis it proved to be benzol and not toluol. It solidified at 0° C. into a crystalline mass resembling loaf-sugar, and could be converted readily into aniline. The transformation which the benzoate of the oxide of methyl undergoes is therefore of a different kind, and there is probably generated olefiant gas, or an isomeric compound, which we did not however collect.

$$\underbrace{C_{16}\,H_8\,O_4}_{\text{Benzoate of methyl.}} + 2CaO = \underbrace{C_{12}\,H_6}_{\text{Benzol.}} + \underbrace{C_2\,H_2}_{\text{Olefiant gas.}} + 2(CaO,\,CO_2)?$$

The metamorphosis observed in the salicylate of the oxide of methyl appears therefore to be peculiar only to the æthers of those acids whose hydrates contain six atoms of oxygen.

Preparation of Toluidine.

We acted upon toluol with concentrated nitric acid, and on the addition of water procured an oily fluid perfectly analogous to nitrobenzide. This substance is nitrotoluide, and when it is dissolved in alcohol, saturated with ammoniacal gas, treated with sulphuretted hydrogen, and then allowed to repose in a corked flask for some days, a beautiful crystallization of sulphur appears, and the liquid loses the smell of sulphuretted hydrogen. It must now be saturated anew with hydrosulphuric acid, and this process repeated until that gas no longer disappears. This method is very convenient, but tedious, as to obtain a sufficient quantity of the base for an investigation two or three months are required. To hasten the process, it is necessary, after each treatment with sulphu-

retted hydrogen, to distil the whole liquid, whereby the deposition of sulphur is quickened, although some of the gas escapes decomposition. After the separation of the sulphur the residue in the retort must be mixed with the distillate, the whole treated again with hydrosulphuric acid, and distilled. This process must be repeated five or six times successively. The decomposition of nitrotoluide by sulphuret of ammonium, as well as the bodies similarly constituted, takes place with great difficulty. Even after a very long exposure to the influence of sulphuretted hydrogen and endless distillations, a small quantity of the nitrotoluid remains intact, which is readily seen by adding water to the treated menstruum, the hydrochloric acid in excess filtering off the sulphur, and agitating the filtrate with æther. On evaporating the æthereal extract, undecomposed nitrotoluide will remain. The dark red acid solution remaining, after draining off the æthereal solution of nitrotoluid, on being evaporated to about one-third of its original volume, in order to expel the alcohol, and then submitted to distillation with sticks of potash, gives off in addition to aqueous vapour and ammonia, a colourless or slightly yellowish oil, which sinks in the receiver and solidifies after some time into a crystalline mass. This body is *a new organic base*, for which we propose the name *toluidine*. Its purification is very simple. The distillate, which was still slightly alcoholic, contained some of the base in solution; we therefore supersaturated the whole with oxalic acid, evaporated to dryness in a water-bath, treated the residue with boiling alcohol, and filtered. The oxalate of toluidine percolates through, while the oxalate of ammonia, which is insoluble in this menstruum, remains. When the filtrate cools, the oxalate of the new base separates almost entirely in fine white needles. These were edulcorated, then dissolved in boiling water and decomposed by a strong potash ley. The base immediately separated in the form of colourless oil-drops, which after some time rose to the surface as an homogeneous layer, and in cooling solidified into a radiated crystalline mass. This was ejected, thrown upon a filter, washed with distilled water until the liquid percolating possessed no more an alkaline reaction, and then desiccated between folds of bibulous paper. The dry crystalline mass required only to be again rectified in order to obtain it chemically pure. During this last process it first melts and then there distils over a beautiful fluid dispersing light in an eminent degree, and which, after some seconds, solidifies into a colourless transparent crystalline mass.

Composition of Toluidine.

The perfect analogy subsisting between benzol and toluol, so evident in every point of view, left in our minds no doubt as to the composition of the new base. We have notwithstanding submitted it to elementary analysis, but have omitted the determination of the nitrogen.

By a combustion with oxide of copper, 0·1955 grm. toluidine gave 0·5630 grm. carbonic acid and 0·1515 grm. water.

Centesimally,—

Carbon	78·53
Hydrogen . . .	8·61

Agreeing with the formula $C_{14}\,H_9\,N$; which we append in a calculated form.

		Theory.		Found.
14 equiv.	Carbon .	1050·00	78·38	78·53
9 ...	Hydrogen	212·50	8·39	8·61
1 ...	Nitrogen .	177·00	13·23	12·86
		1339·5	100·00	100·00

In order to control this formula, we prepared the double compound of the base with chloride of platinum. On igniting this fine crystalline compound, 0·4337 grm. of it gave 0·1372 grm. = 31·36 platinum.

Atomic weight from experiment	1359·50
Atomic weight theoretical . .	1339·50

The formation of toluidine from nitrotoluide is perfectly analogous to that of aniline from nitrobenzide:

$$\underbrace{C_{14}\,H_7\,NO_4}_{\text{Nitrotoluide.}} + 4\,HS = \underbrace{C_{14}\,H_9\,N}_{\text{Toluidine.}} + 4\,HO + 6\,S$$

Properties of Toluidine.

The new base, as previously stated, is obtained in the form of a colourless crystalline mass. From a hot saturated solution in aqueous alcohol it shoots, upon cooling, into large broad plates, which fill the whole menstruum. It dissolves in æther, pyroxylic spirit, acetone, sulphuret of carbon, the fatty and essential oils with the same facility as in alcohol. Water also dissolves a small quantity of toluidine, particularly with heat, and after some time it separates in extremely small leafy crystals, exhibiting a splendid iridescence. On agitating with æther the base is extracted from the water.

Toluidine possesses a vinous aromatic smell and burning taste. The remarkable correspondence as to smell and taste between benzol and toluol, nitrobenzide and nitrotoluide, is also recognised between toluidine and aniline. These bases could

not possibly be distinguished one from the other by smell. Toluidine has no action upon curcuma paper, but it colours green the pigment of dahlias. Reddened litmus paper is faintly blued. Toluidine is heavier than water. It evaporates at all temperatures, and when a glass rod moistened with hydrochloric acid is held over it white fumes are perceptible; this also takes place with nitric acid, but in a less degree. When pressed with the hand between paper it leaves a slight stain, which is however very fugitive. The fusing-point of this base lies at 40° C., the boiling-point exactly at 198° C.

Some years ago Professor Kopp * drew attention to the remarkable relation subsisting between the boiling-points of bodies whose composition differs in a constant number of equivalents of the same elements. He found, for instance, that the difference in the boiling-points of two compounds which differ by two equivalents of carbon and two equivalents of hydrogen (C_2 H_2) is invariably 19° C. Kopp showed this at first by comparing the boiling-points of a vast number of ethyl and methyl compounds, and then the numerous hydrated acids differing in C_2 H_2. Since that time this concurrence between a series of newly-discovered æthers and acids has been perfectly confirmed, but it seems to take place only in bodies of an analogous character, as remarked by Kopp and subsequently by Fehling †.

We possess in benzol and toluol and their derivatives also two series of analogous bodies, whose composition is distinguished by the constant difference C_2 H_2. It was of interest to compare the boiling-points of these bodies in the sense referred to.

	Boiling-point.	Difference.
Benzol	86° C.—Mitscherlich . . .	22°
Toluol	108°.—Deville	
Nitrobenzide	213°.—Mitscherlich . .	12°
Nitrotoluide	225°.—Deville	
Aniline	182°.—A. W. Hofmann . .	16°
Toluidine	198°.—Muspratt & Hofmann	

This comparison shows undoubtedly that Kopp's rule holds good with regard to the above-cited bodies.

The differences evidently arise from mistakes in observation. As for the boiling-points of nitrobenzide and nitrotoluide, the somewhat considerable variation can by nowise surprise, knowing as we do with what readiness bodies of this nature undergo decomposition when submitted to distillation. It is very probable that the boiling-point of nitrotoluide is

* *Ann. der Chem. und Pharm.*, Bd. xlii. p. 79.

† Ibid., Bd. liii. p. 410.

higher, and as for toluol its boiling-point by Deville also does not appear exact.

We will prove in a future paper that dracyl, a hydrocarbon obtained in the destructive distillation of dragon's blood by Bondault and Glénard *, is *identical* with toluol. Glénard and Boudault give as the boiling-point of their liquid 106° C. According to this determination the difference between it and benzol would only be 20°.

From the preceding remarks an uncertainty is removed which has reigned with regard to the boiling-point of aniline, which according to Fritzsche is 228° C.; his product being obtained from indigo. The foregoing statement refers to aniline (cyanol) procured from coal-gas naphtha. It is therefore perfectly clear that there must have been some error in Fritzsche's determination.

Toluidine shares with aniline, and in general with the bases obtained in a similar manner, the property in an acid solution of imparting an intense yellow colour to fir-wood and the pith of the elder-tree. But it does not afford the beautiful reaction with hypochlorite of lime which characterizes aniline; an aqueous solution of toluidine when mixed with liquid chloride of lime gives a pinkish hue. It also differs from aniline in its behaviour towards fuming nitric acid and chromic acid. Toluidine gives with *nitric acid* a fine scarlet colour, whereas aniline assumes an indigo blue tinge.

With *chromic acid* it gives a reddish brown precipitate, which appears to be chromate of toluidine. It does not inflame when brought into contact with crystals of chromic acid.

The following will suffice as to the behaviour of toluidine towards the solutions of the metallic oxides.

Sulphate and chloride of copper give greenish precipitates, possessing a crystalline aspect. *Chloride of iron* deposits hydrated peroxide of iron when heated with toluidine.

Toluidine gives with nitrate of silver a white crystalline precipitate, evidently a double salt, which easily blackens. This base gives with chloride of platinum and chloride of palladium beautiful orange-yellow crystalline precipitates, of which the latter is somewhat lighter than the former.

Toluidine furnishes no particular appearances with other reagents.

Compounds of Toluidine.

The same extraordinary capacity for crystallizing which we have in the salts of aniline also distinguishes those of toluidine.

* *Journal de Pharm et de Chem.*, 3 sér. t. vi. p. 250.

An alcoholic solution of this base solidifies almost immediately when mixed with most acids, and in order to obtain the salts in good crystals it is only necessary to employ water or spirits of wine as the solvent. The compounds are inodorous, and with the exception of the palladium and platinum salt colourless. When they are exposed, particularly in a moist state, to the air, they acquire a pinkish hue like the aniline compounds. They are decomposed by the caustic or carbonated alkalies and ammonia with the greatest facility; the toluidine separating in crystalline grains.

The constitution of the salts of toluidine resembles that of the aniline and ammoniacal salts.

Sulphate of toluidine, $SO_3 + C_{14} H_9 N, HO$.—Toluidine was dissolved in æther and then a few drops of sulphuric acid added, when immediately a shining white crystalline precipitate appeared, which was collected on a filter and edulcorated with more of the solvent. This salt is difficultly soluble in alcohol, but more readily dissolved by æther.

Analysis.

0·4102 grm. of sulphate of toluidine gave 0·3015 grm. of sulphate of barytes = 25·22 per cent. sulphuric acid.

This determination agrees with the formula

$$SO_3 + C_{14} H_9 N, HO,$$

as the subjoined comparison shows.

	Theory.		Found.
1 equiv. Sulphuric acid	500·00	25·60	25·22
1 ... Toluidine . .	1339·50	68·67	
1 ... Water . . .	112·50	5·73	
	1952·00	100·00	

Binoxalate of toluidine, $2 C_2 O_3 + C_{14} H_9 N, HO + 2$ aq.—The salt obtained on mixing a solution of toluidine in alcohol with an excess of oxalic acid is a binoxalate. It appears in silky needles, which are sparingly soluble in cold water and alcohol and quite insoluble in æther. This salt is more readily dissolved by spirits of wine and boiling water. The solution has a strong acid reaction and a saline unpleasant styptic after-taste. The combustion of this compound with chromate of lead afforded the following numbers:—

0·3975 grm. of the oxalate gave 0·7575 grm. carbonic acid and 0·2120 grm. of water.

Centesimally,—

Carbon	51·99
Hydrogen . . .	5·90

The formula of the acid salt is in perfect accordance with the above results, $2\,C_2\,O_3 + C_{14}\,H_9\,N,\,HO + 2$ aq, which we append with the calculated composition.

		Theory.		Found.
18 equiv.	Carbon . . .	1350	52·37	51·99
12 ...	Hydrogen . .	150	5·82	5·90
1 ...	Nitrogen . . .	177	6·97	
9 ...	Oxygen . . .	900	34·84	
		2577	100·00	

In order to verify the formula, we also determined the oxalic acid of the salt by dissolving a portion in boiling water, supersaturating with ammonia and adding chloride of calcium.

0·4835 grm. of binoxalate gave 0·2330 grm. of carbonate of lime = 34·33 per cent. anhydrous oxalic acid.

		Theory.		Found.
2 equiv.	Oxalic acid .	900·00	34·92	34·33
1 ...	Toluidine . .	1339·50	52·01	
3 ...	Water . . .	337·50	13·07	
		2577·00	100·00	

This compound possesses therefore the same constitution as the binoxalate of ammonia. Napththalidine and chloraniline form salts of the same composition.

Hydrochlorate of toluidine, $Cl\,H,\,C_{14}\,H_9\,N$.—It is obtained by evaporating a solution of toluidine in muriatic acid. Upon cooling this salt deposits in scaly crystals, which in a pure state are white, but when exposed to the air assume a yellowish colour. They dissolve copiously in water and alcohol, sparingly in æther. The solution has an acid reaction. When the crystals are slightly heated in a tube they sublime like sal-ammoniac.

Analysis of the salt.

0·3590 grm. of hydrochlorate of toluidine gave 0·3568 grm. of chloride of silver = 25·29 per cent. hydrochloric acid, agreeing perfectly with the formula $Cl\,H,\,C_{14}\,H_9\,N$, which is specified in the following calculated per cents.:—

1 equiv.	Hydrochloric acid	455·15	25·36	25·29
1 ...	Toluidine . . .	1339·50	74·64	
		1794·65	100·00	

Platinchloride of Toluidine, $Cl\,H,\,C_{14}\,H_9\,N + Pt\,Cl_2$.—It is obtained as an orange-yellow spangular mass when toluidine,

hydrochloric acid and chloride of platinum are mixed together. The crystals were washed with a mixture of alcohol and æther and then desiccated in a water-bath. We have already alluded to the determination of the platinum in this salt when speaking of the atomic weight. The analysis gave 31·36 per cent. of platinum.

The formula $ClH, C_{14} H_9 N + Pt Cl_2$ agrees with 31·51 per cent. platinum.

We have not examined the other salts of toluidine, and shall therefore only remark that the nitrate and phosphate are obtained in crystals on bringing the respective acids in contact with toluidine.

Products of the Decomposition of Toluidine.

We should have been exceedingly glad to have submitted toluidine to the action of different agents, but the difficulty of obtaining this body in sufficient quantity prevented us from satisfying our wishes. We can therefore only give a few reactions, which we had the opportunity of remarking during the course of the investigation. When the vapour of toluidine is passed over fused *potassium*, an energetic reaction ensues, and there is formed a quantity of *cyanide of potassium*, as was readily ascertained by the residue giving off hydrocyanic acid when treated with a mineral acid. With concentrated *nitric acid* the base is decomposed, and a large quantity of nitrous acid eliminated. On mixing the solution with water, sulphur-yellow flakes are deposited, which dissolve in alkalies with a brownish-red colour, and reappear on the addition of an acid. This behaviour is analogous to that of nitrophenisic acid, but we are not in a position at present to communicate anything more definite concerning this substance. When this base is treated with a solution of bromine a violent action ensues, accompanied by an elevation of temperature and formation of hydrobromic acid. When the product is heated in a test-tube, there sublimes in the upper part white, shining needles, which are soluble in alcohol and æther, but insoluble in water. They do not possess basic properties, and behave in every respect like tribromaniline; it is highly probable that their composition is also similar. We have not yet procured a sufficient quantity of these crystals in order to verify by experiment the annexed formula,—

$$C_{14}\left\{\begin{matrix} H_6 \\ Br_3 \end{matrix}\right\} N.$$

The effect of chlorine upon toluidine has not been at all studied, but it is highly probable that in this reaction there would

be formed collaterally with trichlorotoluidine derivative products of substitution of anisol.

We possess in the indigo, salicyl and phenyl families, well-examined groups of organic bodies, which are in the most manifold manner connected with each other. There appears to be parallel with these another extended series of corresponding compounds, which differ only in $C_2 H_2$, but as yet there are many interruptions, so that the group of indigo is entirely wanting.

In toluidine we have described one member which hitherto was unknown; the others requisite will also certainly be discovered before long.

The following is a view of these two series of compounds:—

Indigo, Salicyl and Phenyl series.		Anisyl series, &c.	
Indigo	$C_{16} H_5 NO_2$		
Isatin	$C_{16} H_5 NO_4$		
Chlorisatin	$C_{16}\{H_4, Cl\} NO_4$		
Dichlorisatin	$C_{16}\{H_3, Cl_2\} NO_4$		
Salicylic acid	$C_{14} H_6 O_6$	Anisic acid	$C_{16} H_8 O_6$
Bromosalicyl	$C_{14}\{H_5, Br\} O_6$	Bromanisic acid	$C_{16}\{H_7, Br\} O_6$
Dibromosalicyl	$C_{14}\{H_4, Br_2\} O_6$		
Tribromosalicyl	$C_{14}\{H_3, Br_3\} O_6$		
Nitrosalicylic acid, Indigotic acid	$C_{14}\{H_5, NO_4\} O_6$	Nitranisic acid	$C_{16}\{H_7, NO_4\} O_6$
Wanting		Bromonitrasine	$C_{16}\{H_6, Br, NO_4\}$
Phenol, Hydrate of phenyl	$C_{12} H_6 O_2$	Anisol	$C_{14} H_8 O_2$
Bromophenol, Bromophenasic acid	$C_{12}\{H_5, Br\} O_2$	Bromanisol	$C_{14}\{H_7, Br\} O_2$ (?)
Dichlorophenol, Chlorophenissic acid	$C_{12}\{H_4, Cl_2\} O_2$	Dibromanisol	$C_{14}\{H_6, Br_2\} O_2$
Trichlorophenol, Chlorophenissic acid	$C_{12}\{H_3, Cl_3\} O_2$		
Pentachlorophenol, Chlorophenusic acid	$C_{12}\{H, Cl_5\} O_2$		
Dinitrophenol, Nitrophenesic acid	$C_{12}\{H_4, 2NO_4\} O_2$	Dinitranisol	$C_{14}\{H_6, 2NO_4\} O_2$
Trinitrophenol, Carbazotic acid, Nitrophenisic acid	$C_{12}\{H_3, 3NO_4\} O_2$		
Anthranilic acid	$C_{14} H_7 NO_4$		
Salicylous acid	$C_{14} H_6 O_4$		
Benzoic acid	$C_{14} H_6 O_4$		
Nitrobenzoic acid	$C_{14}\{H_5, NO_4\} O_4$		
Benzol	$C_{12} H_6$	Toluol	$C_{14} H_8$
Sulphobenzide	$C_{12}\{H_5, SO_2\}$	Sulphotoluid	(?)
Hyposulphobenzidic acid	$C_{12} H_5 S_2 O_5$	Hyposulphotoluidic acid.	$C_{14} H_7 S_2 O_5$

Indigo, Salicyl and Phenyl series.		Anisyl series, &c.	
Chlorbenzol	$C_{12}\left\{\begin{matrix}H_3\\Cl_3\end{matrix}\right\}+3ClH$	Products of the action of Chlorine upon Toluol.	$C_{14}\left\{\begin{matrix}H_7\\Cl\end{matrix}\right\}$ $C_{14}\left\{\begin{matrix}H_5\\Cl_3\end{matrix}\right\}+ClH$ $C_{14}\left\{\begin{matrix}H_3\\Cl_3\end{matrix}\right\}+2ClH$ $C_{14}\left\{\begin{matrix}H_3\\Cl_5\end{matrix}\right\}+3ClH$ $C_{14}\left\{\begin{matrix}H_2\\Cl_6\end{matrix}\right\}$
Chlorbenzide	$C_{12}\left\{\begin{matrix}H_3\\Cl_3\end{matrix}\right\}$		
Nitrobenzide	$C_{12}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}$	Nitrotoluide	$C_{14}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}$
Binitrobenzide	$C_{12}\left\{\begin{matrix}H_4\\2NO_4\end{matrix}\right\}$	Binitrotoluide	$C_{14}\left\{\begin{matrix}H_6\\2NO_4\end{matrix}\right\}$
Azobenzide	$C_{12}H_5N$		
Aniline	$C_{12}H_7N$	Toluidine	$C_{14}H_9N$
Bromaniline	$C_{12}\left\{\begin{matrix}H_6\\Br\end{matrix}\right\}N$		
Dibromaniline	$C_{12}\left\{\begin{matrix}H_5\\Br_2\end{matrix}\right\}N$		
Tribromaniline	$C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N$		
Chlorodibromaniline	$C_{12}\left\{\begin{matrix}H_4\\Cl_2\\Br\end{matrix}\right\}N$		
Nitraniline	$C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N$		

We have given at the close of the table a body which has not yet been described. This is the *nitraniline*,—

$$C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N,$$

aniline, in which *one equivalent of hydrogen* is replaced by the elements of *peroxide of nitrogen*. In continuing our researches on the substitution products of aniline, and upon which one of us has lately published *, we tried to produce the above compound in a variety of ways, but we have only arrived at a satisfactory result by acting upon binitrobenzide with sulphuret of ammonium.

The new body in which the electro-positive properties of aniline are preserved, crystallizes, affords crystallizable compounds possessing the same constitution as those of aniline, and undergoes distillation without being decomposed. Chemistry has no analogue to nitraniline. It is the first body in which basic properties are recognisable in spite of the entrance of peroxide of nitrogen, and does on this account therefore deserve the attention of chemists.

We shall shortly communicate to your valuable Society our results upon nitraniline. In concluding this treatise we

* Hofmann, Metamorphoses of Indigo.—See page 266.

shall draw attention to a remarkable way for obtaining aniline, and which we discovered during our experiments.

Chemists are well acquainted with the interesting compound Mitscherlich described under the name of azobenzide in one of his beautiful papers upon the derivatives of benzoic acid. He obtained this body by distilling nitrobenzide with alcohol and potash, together with other products which were not further investigated. Azobenzide differs only from aniline in two equivalents of hydrogen.

$$\begin{aligned} &\text{Aniline} \;.\;.\;. && C_{12}\,H_7\,N \\ &\text{Azobenzide} \;.\;. && C_{12}\,H_5\,N. \end{aligned}$$

In order to see if a closer relation did not subsist between these two bodies, we prepared large quantities of azobenzide, following Mitscherlich's directions throughout, and obtained this body, possessing all the properties ascribed to it by that chemist.

On more closely examining the secondary products formed during this process, we found that besides other substances there is likewise produced a very large quantity of *aniline*, and the residue contains a considerable quantity of *oxalic acid*.

These observations appear to shed more light upon the manner in which the azobenzide is formed, *i. e.* if we assume that the oxalic acid is produced from the alcohol at the expense of the oxygen of the nitrobenzide: 2 equivalents of nitrobenzide and 1 equivalent of alcohol contain the elements of 1 equivalent of azobenzide, 1 equivalent of aniline, 2 equivalents of oxalic acid, and 2 equivalents of water, as shown in the subjoined equation,—

$$\underbrace{2\,(C_{12}\,H_5\,NO_4)}_{\text{Nitrobenzide.}} + \underbrace{C_4\,H_5\,O\,HO}_{\text{Alcohol.}} =$$

$$\underbrace{C_{12}\,H_5\,N}_{\text{Azobenzide.}} + \underbrace{C_{12}\,H_7\,N}_{\text{Aniline.}} + 2\,\underbrace{(C_2\,O_3,\,HO)}_{\text{Oxalic acid.}} + 2\,HO.$$

We are far from supposing that the above equation represents the true decomposition, as other products are formed; and further, the aniline distils over long before a trace of oxalic acid is detectable in the retort. The true transformation can only be given when all the products of this complex reaction are investigated. We are at present engaged upon this subject, and expect shortly to solve the problem.

April 21, 1845.—William Thomas Brande, Esq., Vice-President, in the Chair.

Mr. John Thomas Cooper presented a Galvanic arrangement constructed by the late Dr. Wollaston, consisting of a minute pair of zinc and silver elements, capable of heating to redness a fine platinum wire.

George Philips and George Southby, Esqrs., were elected Members.

The following communications were read:—

A note from Professor Liebig, stating that Dr. Hofmann, in continuing his investigations on coal-gas naphtha during the last summer, had proved that leucol and chinolin were identical.

Professor Bunsen communicated the substance of a paper from M. Genth on the discovery of a large quantity of chemically pure oxide of nickel in the scum which arises in the smelting of copper in certain works in Germany. This oxide of nickel, which amounts to upwards of 13 per cent. in the top skimming, is in a peculiar allotropic condition, being insoluble in acids, and possessing a high specific gravity. It communicates, even in a very minute proportion, great brittleness to the metallic copper and its alloys.

A short notice from Dr. Clark was read to the effect, that as lead is the chief poison ever to be apprehended in water, and as its occurrence is not unfrequent where the water has to be conveyed through much length of leaden pipe, it will probably be satisfactory to the Society to learn, that this poison may be entirely removed by means of an effective filter.

CXLII. *On the Conversion of Cane-sugar into a substance isomeric with Cellulose and Inulin.* *By* Thomas Tilley, *Esq., Ph.D., and* Douglas Maclagan, *M.D., F.R.S.Edin.*

WHEN the juice of beetroot undergoes fermentation at temperatures varying from 30° to 40° C., the cane-sugar which it contains is at first converted into sugar of grapes, and after some time into mannite, lactic acid and a gummy substance, having a composition identical with that of gum-arabic. This is remarkable, inasmuch as it affords an instance of what may be called a retrograde chemical action, the sugar being converted into dextrine,—a change similar to that which occurs in fruits when they lose their sweetness, and assume that condition commonly called "sleepy." The conversion of cellulose into dextrine and sugar seems to be a process of continual occurrence and great importance in the vegetable œconomy, but we are not aware of any example of the reverse of this action, except those instances mentioned above; in the former of which sugar is converted by fermentation into a body having all the properties and composition

of gum; in the latter, the sugar being changed into cellulose*. We therefore consider the observation we are about to describe to be possessed of some interest, as affording another case of a similar retrograde action. It has been observed that the effervescing drinks known as lemonade, gingerade, &c., made by forcing carbonic acid gas into solutions of sugar variously flavoured with tartaric acid and essential oils, in certain cases lose their fluidity, and assume a thick, slimy consistence. When the bottles containing these thickened liquids are opened, the expansion of the carbonic acid expels their contents with difficulty, owing to their extreme tenacity. Instances of this change are of continual occurrence, all the manufacturers of whom we have inquired having observed it when the bottles had been kept for some time. Various opinions have been expressed by them as to the cause of the conversion, but it seems to occur invariably when the liquor is kept long enough. We are indebted to Mr. Baildon of this city (Edinburgh) for an opportunity of examining a sample of gingerade, in which this thickening had occurred. This liquid is made by sweetening an infusion of ginger-roots with cane-sugar, and flavouring it with oil of lemons and tartaric acid; this is then placed in bottles, and carbonic acid forced by pressure into the fluid. Another manufacturer uses the following ingredients in the preparation of effervescing lemonade:—2 ounces of honey, 4 pounds of sugar, 2 ounces of citric acid, 2 drachms of oil of lemons and $1\frac{1}{2}$ ounce of bicarbonate of soda. According to the opinion of this manufacturer, the change occurs chiefly in winter, when the liquid is exposed to cold, and he thinks that the addition of a double proportion of honey tends to prevent it. To separate the substance to which the viscidity was owing, the contents of a bottle were digested with six or seven parts of alcohol, under the action of which the gummy matter consolidated, and when dried became so hard as to be pulverizable. After being powdered, it was again digested and washed with alcohol until nothing more was dissolved. When dried at 100° C. it had the appearance of a semi-transparent horny substance, and was sufficiently elastic to render pulverization difficult. The alcohol contained in solution a quantity of sugar of a brownish colour, quite uncrystallizable, and rendered sour by the presence of the acid used in the manufacture.

The gummy substance treated with cold water slowly reassumes its original appearance. When treated with a large quantity of boiling water it forms a mucilage, which filters with difficulty. Iodine produces no effect on the solution.

* See Mulder's *All. Phys. Che.*, p. 243 *et seq.*

Subjected to Trommer's test for dextrine, sugar and gum, this did not indicate the presence of any of these substances. With nitric acid it produces oxalic acid. It gives a precipitate with diacetate of lead. It contains, after having been washed with alcohol, a small quantity of ashes, amounting to 1·37 per cent. It was analysed in the usual manner.

I. 0·746 of substance gave, with oxide of copper and chlorate of potash, 4·070 HO and 1·1735 CO_2 = 0·04727 H and 0·32448 C.

II. 0·1525 of substance gave 0·092 HO and 0·232 CO_2 = 0·010222 H and 0·06474 C.

These numbers, allowance being made of the ashes, give the following proportions:—

	I.	II.	Atoms.	Calculated.
Carbon . .	43·80	43·31	24	43·71
Hydrogen .	6·14	6·80	21	6·25
Oxygen . .	50·06	49·89	21	50·04

From this it would appear that this gummy substance is isomeric with cellulose and inulin*.

This substance, which has a composition similar to cellulose and inulin, is evidently formed from the cane-sugar in the lemonade, as all its other constituents exist in too small quantity to admit the idea of their having been its origin.

2 atoms sugar	C 24	H 22	O 22
1 ... water		H	O
1 ... gummy substance	C 24	H 21	O 21

This substance is formed then from 2 atoms of sugar by the abstraction of 1 atom of water.

As a solution of the gummy substance gave a compound with lead, we endeavoured to obtain by its aid its atomic weight. 0·260 of the precipitate gave of lead and oxide of lead quantities equal to 0·316 oxide of lead, which, when allowance is made for ashes, is equal to 55·8 per cent. of oxide of lead. We had not enough of the salt to enable us to make the combustion, but have calculated the formula from the quantity of lead.

* Cellulose, Payen. Endine.

Carbon .	43·40
Hydrogen	6·12
Oxygen .	50·38[a]

Inulin. Parnell.

Carbon .	43·95
Hydrogen	6·30
Oxygen .	49·75[c]

From turnip. Fromberg.

Carbon .	43·95
Hydrogen	6·13
Oxygen .	49·66[b]

From Dahlia root. Payen.

Carbon .	44·19
Hydrogen	6·17
Oxygen .	49·64[d]

[a] *Ann. de Sc. Nat.*, 1840, p. 73. Bot. [b] Mulder, *Op. cit.*, p. 203.
[c] *Ann. der Chem. und Pharm.*, Bd. xxxix. S. 213. [d] *Op. cit.*, p. 91.

		Atoms.	Calculated.
Carbon .	19·31	24	1834·4 = 18·7
Hydrogen	2·76	21	260·0 = 2·7
Oxygen .	22·11	21	2100·0 = 21·4
PbO . .	55·80 found	4	5578·0 = 57·1

From 55·8 per cent. oxide of lead the atomic weight found is 4400·0. The calculated one is 4198·4.

We had imagined that this curious change in sugar might have been the effect of organization, but our friend Mr. John Goodsir was kind enough to examine the substance, and informed us that he could discover no trace of organization.

CXLIII. *On the Action of Bleaching Powder on the Salts of Copper and Lead. By* Walter Crum, *Esq., F.R.S.*

IN February 1843 I read to the Philosophical Society of Glasgow an account of a rose-coloured oxide of copper which I had obtained by the action of bleaching powder and lime upon nitrate of copper. Although I had then made numerous analyses of this substance, prepared under a variety of circumstances, I had been unable to obtain from it the full amount of oxygen which a definite compound must contain, and delayed therefore to make it further known until I should have the opportunity of producing it in a purer form. In the mean time the rose-coloured substance was observed, and correctly described, by Krüger of Berlin, as a combination of the oxide of copper, or, as he calls it, cupric acid, with lime. Having completed my experiments on this subject as far as my leisure will permit, I shall now state the results I have obtained.

When the hydrated oxide of copper is added to a solution of bleaching powder it changes colour and becomes brown. Oxygen gas is then plentifully disengaged, and the effervescence continues till the whole of the hypochlorite of lime is decomposed. The brown precipitate suffers no change during this decomposition. When separated from the soluble matters, it is found to contain no chlorine and no excess of oxygen. It is anhydrous oxide of copper. Hypochlorite of soda produces the same effect.

If we add nitrate of copper to a solution of bleaching powder containing a considerable quantity of lime, and previously cooled to below the freezing-point of water, a bluish-green precipitate is formed. When the precipitate subsides, we find the solution of a fine blue colour and containing copper; but in what state I have not examined. As the heat advances to the ordinary temperature, the copper in solution, as well as

the precipitate, changes colour, and both at last become an insoluble purplish black powder. Oxygen gas is disengaged during the latter part of this process, and continues for some time to prevent the precipitate from subsiding; but after twenty or twenty-four hours the evolution of gas nearly ceases, the particles having united into larger grains sink to to the bottom of the vessel into moderate bulk, and may then readily be separated from the soluble matters, by repeated mixing with cold lime-water and drawing off the clear liquid with a syphon. The precipitate thus obtained is, as I have said, nearly black; but by triturating upon a piece of glass it is seen that its real colour is rose-red.

Exposed to the action of boiling water oxygen gas is disengaged from this substance, and brown anhydrous oxide of copper is left behind. Acids dissolve it, with the liberation of oxygen gas, mixed with the carbonic acid taken down by the lime. The solution in nitric acid gives no precipitate with nitrate of silver. Exposed to the air the substance is speedily changed into the green carbonate. In attempting to press and then to dry it *in vacuo* over sulphuric acid, a large proportion was changed into the brown oxide mixed with carbonate. It can only therefore be examined in the moist state and newly prepared. I shall describe the process by which I have obtained the best results.

Twenty grains of black oxide of copper, prepared by calcining the nitrate, are dissolved with the assistance of heat in 70 grs. of nitric acid, specific gravity 1·35. Fifty grains of fresh hydrate of lime, sifted through fine calico, are mixed with 1 lb. solution of bleaching powder of specific gravity 1·06, and added to the solution of copper. When the precipitate becomes granular, as already described, it is quickly washed, and decanted until the lime water comes off nearly pure. The precipitate is then put into a wide tube over mercury, an excess of sulphuric acid added to it; and, after pouring out as much as possible of the solution which is thus formed, caustic soda is added to absorb the carbonic acid. In six experiments made in this way, 20 grs. of oxide of copper produced a compound which yielded of oxygen gas, after the necessary corrections,—

	1·875
	1·886
	1·748
	1·915
	1·795
	1·747
Mean . .	1·828 grain.

By calculation 20 grains CuO changed into $Cu_2 O_3$ ought to yield, by Berzelius's numbers, 1·98 grain of oxygen. A nearer approximation than in the foregoing results is scarcely to be expected; for although there was no perceptible disengagement of gas during the washing of the precipitate in these experiments, it is certain that oxygen always escapes during the time so employed.

The quantity of lime necessary to the production and stability of this oxide is not more than 1 equivalent after saturation of the nitric acid: 1 atom of lime to 3 of copper gave only 0·558 gr. of oxygen gas instead of the mean quantity of 1·828; 2 atoms to 3 of copper yielded 1·295. I conceive the rose-coloured powder then to be a compound of an oxide of copper with lime, in which the copper exists in the state of sesquioxide, $Cu_2 O_3$.

I have not succeeded in producing this oxide by means of the hypochlorites of potash or soda, even with the alkali in great excess; but by adding caustic soda to a solution of hypochlorite of lime, and afterwards nitrate of copper, we obtain the calcareous compound (lime being precipitated along with the copper) in a state of division so fine as to show the rose colour as soon as it is formed. This method, however, does not serve for the purposes of analysis, for the powder never becomes granular, and remains therefore too bulky to be washed.

It will now be observed that the dehydrating action of the hypochlorites upon oxide of copper must depend upon the momentary formation of a sesquioxide in which the oxygen has replaced the previously combined water.

The solution of bleaching powder in which the sesquioxide has been formed is of a fine but very pale pink colour, and contains so small a proportion of the colouring ingredient, that the nature of that body can scarcely be discovered by analytical means. The second washing of the oxide is colourless; but if a very minute portion of sulphate of manganese be added, the pink colour is restored. When manganate of potash is dropped into nitric acid, the well-known red colour of hypermanganic acid is produced. In lime water the colour is bluish green; but in bleaching liquor, even with excess of lime, we have the peculiar amethystine colour of the solution in which the sesquioxide of copper has been produced. Bleaching powder has long been said to contain manganese, and to this I at first attributed the pink colour of the original solution; but I afterwards found that it could be reproduced from pure Irish limestone which I employed. Even marble gives a pink solution in the same circumstances.

The vessel in which the sesquioxide has been produced, is lined with a beautiful rose-coloured deposit, which remains attached to the glass when the other matters are washed out; but it fades away in a few hours, particularly when exposed to light, and cannot even be long preserved in the solution which forms it. Dissolved in dilute nitric acid, copper is found in the solution and no manganese. There can be no doubt that, like the precipitate, it is the sesquioxide of copper in combination with lime.

The red oxide of iron has also the power of decomposing the hypochlorites. This fact, as well as the formation of a superoxide of copper, was observed many years ago by Mr. Mercer of Oakenshaw, and stated by him to the British Association in 1842, in a paper containing some interesting speculations on these and other weak affinities which give rise to many of the phænomena of catalysis.

When a solution of bleaching powder is mixed with nitrate of copper, a light bluish-green powder precipitates, the bulkiness of which renders it somewhat difficult to wash. This powder is very slightly soluble in water, and scarcely changes colour in boiling. Heated in a glass tube over a spirit-lamp, chloride of copper sublimes into a cooler part of the tube, and water escapes. The residue consists of black oxide of copper mixed with a quantity of chloride, which may be separated from the oxide by washing. Professor Graham, who suggested to me this experiment, remarked the analogous effect of boiling water in separating water from a hydrate. It proved to be a hydrated oxichloride of copper, the substance known by the name of Brunswick green, and formed in a variety of other circumstances. Analysis gave me nearer $3\,CuO,\ CuCl$ than $4\,CuO,\ CuCl$; but the presence of carbonate in the specimen left me in doubt upon this point, and I could not resume the inquiry. In this reaction the whole of the hypochlorous acid is set free.

$$\begin{aligned} &4(CuO\ NO_5) + 3(CaO\ ClO,\ CaCl) \\ &= 4(CaO\ NO_5) + 3\,CuO,\ CuCl + 2\,CaCl + 3\,ClO. \end{aligned}$$

Peroxide of lead is often produced by passing a stream of chlorine through a solution of sugar of lead. The chloride which accompanies it in this way may be also converted into peroxide by employing a solution of bleaching powder instead of chlorine. The peroxide produced by these means has a light brown colour, although washed with dilute nitric acid and boiling water. I have succeeded, by the following process, in forming a compound, nearly colourless, of *peroxide of lead and lime*. Dissolve in water 1 lb. of nitrate of lead,

and add it, along with 3 equivs. of lime, to 16 pounds of a solution of bleaching powder of sp. gr. 1·08. Heat the mixture gradually to 160° Fahr. and stir it frequently during five hours. Pour off the clear liquid, add 16 pounds more of the same solution, and continue the heat three hours longer. The combination is obtained white with only a slight brown tinge. It is quite insoluble in water, and when dried does not alter in the air. Nitric acid, by dissolving the lime, leaves the peroxide of a deep black colour, and therefore much deeper than that obtained by any of the processes usually employed.

I have had no means of determining the proportion of lime contained in this plumbate. With less than two equivalents to one of oxide the compound is not white; and an excess of lime cannot afterwards be dissolved away by an acid without discolouring the salt.

I found it convenient in these experiments to prepare a quantity of cream of lime, by dropping newly-burnt lime into boiling water, stirring up, allowing the sand and the grosser parts to subside, and pouring off the superstratum. When this again had subsided for some time, the water was poured away, and the cream of lime which remained corked up in small bottles for use. By this means I had always at hand a quick lime, whose equivalent I knew, free from sand and free from carbonate. Marble, of course, answers the best for this purpose.

Manganese, again, appears in the nitric acid which has been employed to decompose the plumbate, in the state of a pink-coloured hypermanganic acid. When this solution is poured off and more water and nitric acid added to the peroxide that is left, a small quantity of sulphate of manganese restores the colour. Peroxide of lead, prepared by the same or by other means, when dried, does not yield the pink colour without the application of heat.

May 5, 1845.—The President in the Chair.

Thomas Dell, Esq., was elected a Member of the Society.

The following papers were read:—

An abstract from a Letter from Professor Bunsen of Marburg, stating that he had undertaken some experiments on the direct formation of cyanogen from the union of the nitrogen of the air with carbon. Two experiments were made with carbonate of potash and charcoal from pure sugar, in iron tubes heated to whiteness, through one of which nitrogen was led, through the other carbonic acid. In the first experiment there was a yellow-red flame on igniting the gases, and which smelt strongly of cyanogen; there was also abundant vapours of cyanide of potassium: the contents of the tube gave

upwards of 6 grammes of cyanide of silver, free from chloride. In the second tube the gases were perfectly free from cyanogen, burnt with a pale blue flame, and no cyanide of potassium could be detected in the mixture. The reason of previous failures was the absence of a sufficiently intense heat.

CXLIV. *Note on the Existence of Phosphoric Acid in the Deep-Well Water of the London Basin. By* Thomas Graham, *Esq., F.R.S.*

THIS water is obtained on piercing the London clay, which forms an impervious bed, generally exceeding 200 feet in thickness, and flows from fissures in the subjacent chalk. It is always highly soft and alkaline, and remarkable for the predominance of soda salts over earthy salts among its solid constituents. I have never found it to contain a sensible quantity of potash, although salts of the vegetable alkali appear among the constituents of the water of the deep Artesian well of Grenelle.

When evaporated considerably, a small deposit takes place in the London deep-well water, which consists chiefly of carbonate and phosphate of lime. The remaining liquid gives with nitrate of silver a precipitate of chloride and carbonate of silver, which is white without any shade of yellow; but if a portion of the water, amounting to an ounce or two, be evaporated to dryness in a platinum capsule, without removing the precipitate, and the heat afterwards continued so as to raise the temperature of the resulting dry saline matter to low redness, then, on redissolving by distilled water, and adding nitrate of silver, a precipitate is obtained, in which the yellow colour of the phosphate of silver is very perceptible. The earthy phosphate is decomposed by ignition with the alkaline belonging to the water, and the soluble phosphate of soda is produced.

The following are the results of the analysis of the water from the deep well in the Brewery of Messrs. Combe and Delafield, Long Acre. An imperial gallon of the water contained 56·45 grains of solid matter, 100 parts of which gave—

Carbonate of soda	20·70
Sulphate of soda	42·94
Chloride of sodium	22·58
Carbonate of lime	10·96
Carbonate of magnesia	1·92
Phosphate of lime	0·34
Phosphate of iron	0·43
Silica	0·79
	100·66

The growth of green confervæ in this water is extremely rapid, and occasions inconvenience when the water is kept in open tanks. It is a subject perhaps worthy of inquiry, whether the value of some waters for irrigation may not depend upon their containing phosphoric acid, this constituent having hitherto been generally overlooked in waters.

CXLV. *On a Crystallized Alloy of Zinc, Iron, Lead and Copper.* *By* Warren De la Rue, *Esq.*

THE alloy in question was obtained from the worn-out amalgamated zinc plates used in the voltaic battery after the mercury had been recovered by distillation. As the sulphate of zinc, resulting from the solution of the zinc in the battery, is exceedingly pure, it follows that the residue of the plates contains, besides the mercury used for amalgamation, most of the impurities contained originally in the whole plates, and the metal obtained therefrom is consequently much inferior in quality to the original rolled zinc.

Zinc in a fit state for rolling is obtained by running off the fluid portion from a mass of cast zinc which has been allowed to cool down to a certain point after fusion, the metal left behind being less pure than that which flows off. The manufacturer who furnishes me with rolled zinc and takes back the zinc obtained from the worn-out plates, informed me that the latter is unprofitable to re-work from its leaving an unusually large residue in refining; this statement induced me to investigate the composition of this residue, and I proceeded in the following manner.

About 22 pounds of worn-out plates being introduced into an iron pot, and the mercury distilled off by heating it to redness, the fused metal was fined by adding a quantity of tallow and stirring well; after the oxide had been withdrawn the metal was removed to another vessel to cool; it weighed about 15 lbs. When partially solidified the fluid portion was drained off, leaving a considerable portion of the metal in a spongy state, and occupying the same bulk as the whole mass; one part of zinc plate residues usually gives the following results:—

Zinc	·673
Mercury	·043
Dross and loss . .	·284
	1·000

this average being taken on a quantity of old plates amounting to $2\frac{1}{2}$ hundred weight.

The spongy residue, examined with the microscope under a power of twenty to fifty times linear, proved to be composed

of minute, perfectly clean and well-formed crystals of the form of right rhombic prisms; their breadth varying from the $\frac{1}{600}$th to $\frac{1}{300}$th of an inch; the angles of the base are of about 119° and 61° respectively.

A selected portion, free from scoria, weighing 5 grammes, was subjected to analysis, and found to be an alloy of zinc, iron, lead and copper. After solution in nitric acid the lead was separated as sulphate, which weighed ·441 grm.

The copper being precipitated by sulphuretted hydrogen and then converted into oxide weighed ·09 gramme. The iron being thrown down as succinate from the neutralized solution, and after the removal of the soluble salts, washed with ammonia, and ignited, there resulted ·1847 gramme of peroxide of iron.

The zinc, precipitated by carbonate of soda, gave when ignited 5·6213 grammes of oxide of zinc.

These results give the following composition of the alloy:—

	Grammes.		Per cent.
Zinc	4·500	=	90·
Iron	·128	=	2·56
Lead	·300	=	6·
Copper	·072	=	1·44
	5·000		100·00

These quantities agree very exactly with the following formula:—

	Per cent. Calculated.	Per cent. Found.
240 Zn =	89·99	90·
8 Fe =	2·52	2·56
5 Pb =	6·02	6·
4 Cu =	1·47	1·44

It is possible that these substances may be combined into proximate constituents, and the alloy be a compound of these, but we have no data for so grouping them. On re-melting, however, a portion of these crystals, the mass separated into two portions,—a metal considerably more fluid, and a compound more infusible than the crystals; these I have not examined.

From the preceding analysis, it will be seen that a portion of alloy amounting to but 10 per cent. is capable of retaining in combination 90 per cent. of zinc: this will account for the large portion of difficultly fusible metal in a pasty state which frequently rises to the top of the melting-pot in fusing commercial zinc, and which is probably an alloy of zinc combined with but a small portion of other metals.

May 17, 1845.—The President in the Chair.

Mr. Button presented a specimen of rectified Rangoon Naphtha, and an oily fluid obtained during the process of its rectification.

Mr. De la Rue presented a specimen of the Alloy of Zinc, &c., the subject of the communication read at the previous Meeting.

The following papers were read:—

CXLVI. *Some Experiments on Ozone.* *By* A. W. Williamson, *Esq.*

IT has been satisfactorily proved by Marignac*, that the phænomena attributed to ozone have no connexion with the presence of nitrogen. He finds that the ozone odour may be developed in liquids free from nitrogen as well as in those which contain that element. He decomposed by the voltaic current a portion of water from which atmospheric air was carefully excluded, and found that the peculiar smell of ozone was given off, as abundantly after a continuance of the action for several days, when a quarter of the liquid had disappeared in the form of gas, as at the beginning of the decomposition. Marignac confirms Schönbein's statement, that the odorous matter in air acted upon by phosphorus, is identical with that present in the oxygen set free by the electrolytical decomposition of water; and indeed recommends, as the most convenient way of preparing ozone, to pass atmospheric air over phosphorus. The substance made use of in his researches was thus prepared.

The object of the experiments I am about to describe was to obtain some explanation of the phænomena which gave rise to the supposition of the existence of such a body as ozone. The poles of a Bunsen's battery, consisting of four elements, were plunged into sulphuric acid diluted with three volumes of water. The hydrogen from the copper plate at which it was evolved was allowed to escape into the atmosphere. The oxygen which was evolved upon a plate of platinum was collected in a small tubulated glass bell placed over it, and two-thirds sunk in the liquid. Hence it was conveyed into a tube filled with chloride of calcium, through which it passed without any diminution of its peculiar smell. The oxygen thus dried was conducted into a glass tube filled with copper turnings and heated to redness. At the further end of this tube, which was kept cool, globules of water soon made their appearance, which on being removed were speedily reproduced, and continued increasing so long as the process lasted. The oxygen, on entering the tube full of copper, being quite dry,

* *Comptes Rendus à l'Académie*, Mars 1845.

it thus appears that water is formed by the reducing action of the heated metal.

In the manner of performing this experiment, there are two circumstances which take from the result the certainty of correctness necessary for drawing conclusions. These circumstances are the following:—

1st. The copper turnings having, by heating to redness in the air, been covered with a coating of oxide, were reduced by means of a current of hydrogen gas, and although the excess of that gas had been removed as far as possible by a current of dry atmospheric air, yet it was possible that some hydrogen might adhere to the porous copper, which would account for the formation of water on oxygen being brought to the hydrogen at a red heat.

2nd. Hydrogen being somewhat soluble in water, the oxygen may in passing through the liquid have taken up some traces of that element, and on coming in contact with the heated metal the two gases would combine.

To obviate the first of these objections, the oxidated copper was reduced by a current of dry carbonic oxide gas, and to remove the possibility of free hydrogen being carried over with the oxygen, the latter was passed through a tube filled with spongy platinum, and then again over chloride of calcium. It was, however, found that the substance producing the peculiar odour was either decomposed or absorbed by the platinum, none of it passing over.

The difficulty was at length avoided by evolving the oxygen from a liquid in the decomposition of which no hydrogen is set free. Oxide of copper dissolved in sulphuric acid was decomposed instead of water. The oxygen then evolved possessed precisely the same odour as that from acidulated water, and after careful drying was conducted into the heated tube containing copper turnings reduced by carbonic oxide.

Water speedily appeared at the cool end of the tube, and the quantity continued increasing as long as the process lasted.

In subsequent experiments, oxygen prepared in the manner just described was dried and passed through a small glass tube heated to redness by a spirit-lamp; on coming out of which it had completely lost all odour. At the end of this tube a chloride of calcium tube was then fixed, which had been accurately weighed.

After the oxygen was conducted for a short time through the heated tube, the chloride of calcium tube was found to have increased perceptibly in weight.

Water through which oxygen charged with ozone was allowed to pass assumed the odour of it. When this solution of

ozone was added to a solution of iodide of potassium and starch, a pale blue colour was produced; ferro-cyanide of potassium containing ozone gave a blue precipitate with a proto-salt of iron. Lime water formed with the solution of ozone a heavy and apparently crystalline precipitate. Baryta water behaved in a similar manner. The liquid after the precipitation gave no reaction with iodide of potassium and starch; but on an acid being added, a blue colour immediately appeared. The odour did not reappear.

Oxygen charged with ozone was next passed through a tube surrounded by a frigoric mixture consisting of chloride of calcium and snow; but nothing perceptible was deposited.

The following experiments were made for the purpose of ascertaining whether, as has been assumed, the substance causing the ozone odour is also produced by the action of phosphorus on atmospheric air.

Through a glass tube filled with pieces of phosphorus a current of moist atmospheric air was driven by means of a gasometer; it assumed the peculiar odour so well known to accompany phosphorus. Water, through which this air was then allowed to pass for a considerable time, remained inodorous, gave not the slightest reaction with iodide of potassium and starch, left ferro-cyanide of potassium unchanged, and gave all the reactions of a dilute solution of phosphoric acid.

On repeating this experiment it was performed in a somewhat different manner. The air which had passed over phosphorus was allowed to pass directly into the iodide and starch, and a deep blue reaction soon ensued in that part of the liquid on which the bubbles in passing through first acted; and was increased, in a greater proportion to the air passing through, when a rapid current of air was driven over the phosphorus instead of a slow one. On again, as in the former instance, passing the air through water and then treating the latter with iodide of potassium and starch, no reaction was obtained. We have here an evident difference between the reactions of the substance contained in the electrolytic oxygen and that produced by the action of phosphorus on atmospheric air. To what then is to be attributed the reaction produced by the direct action of air passed over phosphorus on iodide of potassium and starch? The following experiment was made. In a long and wide tube loose pieces of asbestos and pieces of phosphorus were placed alternately. By heating the tube thus filled the phosphorus was partly melted into the asbestos, and partly sublimed upon it; thus exposing a far greater surface than in the former experiments.

After the tube had completely cooled, atmospheric air was

driven through it into the iodide and starch, but not the slightest reaction was produced.

This result plainly indicates the cause of the reaction in the preceding instance. The phosphorus was there unable for want of sufficient surface to absorb all the oxygen of the air passing over it. A mixture of phosphoric acid and oxygen therefore went over, and by their simultaneous action on the iodide of potassium set iodine free. As soon as a sufficient surface was given to the phosphorus all oxygen was absorbed, phosphoric acid was alone carried over by the nitrogen, and the iodide was decomposed in a different manner.

Lime water, through which the air thus treated with phosphorus was passed, deposited a voluminous sediment, consisting of phosphate of lime. This liquid cleared by a few drops of acid remained afterwards unclouded on being heated with chloride of mercury: it consequently contained no phosphorous acid. With iodide and starch it gave no reaction, either alone, or after an acid was added to it.

These experiments appear to me to show,—

I. That the peculiar properties belonging to the oxygen set free by the agency of the electric current are produced by the admixture of a *peroxide or acid of hydrogen*;

II. That by the action of phosphorus on atmospheric air the same substance is *not* produced.

That this compound of hydrogen and oxygen is not identical with Thénard's peroxide, would appear from the fact of its being volatile and odorous, properties which the other does not possess. I have repeatedly prepared Thénard's peroxide of hydrogen by decomposing peroxide of barium with different acids, for the purpose of satisfying myself whether it ever possesses odour, but have always obtained a negative result. The oxygen disengaged from it by the action of peroxide of manganese is as inodorous as the liquid itself. The oxygen obtained by the electrolytical decomposition of an aqueous solution of peroxide of hydrogen possesses the same odour, only apparently in a somewhat greater degree, as that from water.

The bleaching action which the substance contained in electrolytical oxygen produces when dry on litmus paper, is a fact which of itself indicates that it must be a peroxide. It is well known that chlorine does not possess that property, but only such combinations of oxygen as give up this element with great ease, as for instance hypochlorous acid.

I cannot conclude this notice without expressing the obligation I am under to Professors Liebig and Buff for their kind direction and assistance during these experiments.

CXLVII. *On the Solubility of Oxide of Lead in Pure Water.* *By* Lieut.-Col. Philip Yorke.

IN the Philosophical Magazine for August 1834, I published a paper on the action of water and air on lead. Some of the principal results contained in it were confirmed by Bonsdorff in two papers; he found that 7000 parts of pure water free from access of carbonic acid dissolved one of oxide of lead; my experiments gave $\frac{1}{12,000}$th to $\frac{1}{10,000}$th. Since that time two papers have appeared on the same subject, one by Dr. Christison*, and one by Mr. R. Phillips, Jun.† The last-named chemist considers that the oxide of lead is not dissolved, but merely mechanically suspended in the water, because the liquid is deprived of the lead by passing it through a paper filter. It is to this opinion that I propose to direct attention in the present notice.

The fact that the aqueous solution of oxide of lead would not pass through a filter was noticed by me in the paper already referred to; but as the action of tests on the liquid was just what one observes with solutions; as no time allowed for subsidence made any difference in these appearances; as the liquid deposited crystals of oxide of lead not only on the lead but on other bodies; as when decomposed by the voltaic battery it gave metallic lead at the negative pole, and peroxide at the positive; I did not consider that the stoppage of the oxide of lead by the filter was any proof of its not being dissolved. There still, however, remains this question to be answered,—In what way does the paper act in retaining the oxide? and I think that the following experiments afford an answer to the question.

I placed some clean rods of lead in bottles of distilled water loosely stopped; in this way, after removing the rods of lead, I obtained a clear liquid, which, when tested by sulphuretted hydrogen, gave a deep brown colour. On passing this liquid through a double filter, which had been previously washed with hot distilled water, it appeared to be very nearly deprived of lead: when two or three fluid ounces had passed through, the filters were removed, washed, then immersed in a solution of sulphuretted hydrogen, again washed and dried. Some torn fragments of the filters were then mounted in Canada balsam for examination by the microscope. On examination with powers of from 150 to 400, the fibres of the flax composing the paper were seen to be browned, and in many instances it could be distinctly observed that the colouring sub-

* Transactions of the Royal Society of Edinburgh.

† Pharmaceutical Journal for December, 1844.

stance occupied the interior of the tubular fibre. Now, it is stated by Mr. Crum, in the Philosophical Magazine for April 1844, that cotton wool possesses the power of abstracting the oxide of lead from its solution in lime-water, and that this property is made available in the processes for dyeing cotton with the chromates. I found that on filtering a solution of oxide of lead in lime water through a triple filter, that whereas the original solution gave a deep black when tested by sulphuretted hydrogen, the filtered liquid gave but a pale brown; and it required that the unfiltered liquid should be diluted with thirty times its volume of water to produce the same test as the filtered.

I then tried the effect of mere immersion of the paper in the aqueous solutions before used. A bit of filtering-paper ten inches by two inches was boiled in distilled water and then put into an ounce phial filled with the aqueous solution; after remaining six hours the liquid was poured off and tested: it gave a pale brown, and it required that the liquid which had not been in contact with the paper should be diluted with ten times its volume of water to produce the same tint. This experiment was repeated with a stronger solution of oxide of lead in water, the water was poured off at the end of four hours; it then gave a pale brown, and it required that the original liquid should be diluted with four times its bulk of water to produce the same tint. A fresh portion of the same solution was then poured on the same paper and left for a night; then, on testing, the liquid gave a brown tint, barely perceptible, and it required that the original liquid should be diluted with from fifteen to twenty times its volume of water to produce the same.

From these experiments it is clear that the effect in question is dependent on a power possessed by the paper in common with several other porous bodies and organised fibres, of separating certain substances from their solutions, a power sufficiently well known, though little understood*. In considering this view of the subject in the present instance, there is a circumstance of some practical importance which it would appear ought to follow, viz. that after the fibres of the paper had been saturated with the oxide of lead, then this substance should pass through in solution. To ascertain whether this was the case I made the following experiments.

I obtained a strong aqueous solution of oxide of lead by immersing slips of clean lead in about three quarts of distilled

* The effective filter mentioned in Dr. Clark's Notice, page 384, is formed of well-washed sand, and has been in use during twelve months without any apparent diminution of power.

water, contained in a two-necked bottle, through which oxygen gas was passed and maintained in contact with, under a slight pressure. In this manner I procured a solution which when quite clear yielded $\frac{1}{7300}$th of ignited oxide of lead. A filter of paper rather less than $\frac{1}{200}$th of an inch thick and four inches in diameter was prepared and washed; then, by fitting into one of the two necks of the bottle a siphon with equal legs, so as to resemble Gay-Lussac's apparatus for washing filters (except that I used a contrivance to prevent the necessity of the air supplied to bottle from bubbling through the solution), I was enabled to allow the filtration to go on with considerable regularity for many hours. The first portion of liquid which passed through gave a pale brown when tested; when nine fluid ounces had passed through the effect was the same as at first, and a portion (*a*) was reserved for future comparison. When forty fluid ounces had passed through, the liquid, which was quite clear, gave a much darker tint with the test than any which had previously been obtained in the experiment. It gave a tint about equal to that given with the unfiltered liquid when diluted with its own volume of water; while it (*i. e.* the last filtered portion) required to be diluted with twice its volume of water to produce the same tint as that given by the reserved filtered portion (*a*). The liquid now passed through the filter very slowly; it was tested again, when eight more fluid ounces had passed through, with the same result as before, except that the tint was a trifle darker.

This experiment sufficiently shows that the effect contemplated does occur, and that it would be unsafe to trust to the action of a filter to separate oxide of lead from water for an unlimited time.

CXLVIII. *On Atomic Volume and Specific Gravity.* *By* Lyon Playfair, *Esq.*, *Ph.D. and* J. P. Joule, *Esq.*

Section I.

THE discovery of Gay-Lussac, that gaseous bodies combine in equal or in multiple volumes, and that the resulting compounds stand in a similar simple relation to their constituents, is one of the most important discoveries ever made in physical science. Its utility has been diminished by its supposed inapplicability to liquid and solid bodies, as its own exactitude at different temperatures is entirely owing to the equal expansibility of the same volumes of different gases by equal increments of heat.

In its most simple form, therefore, it was *à priori* impro-

bable that the law of Gay-Lussac should apply to the liquid and solid forms of matter. But, as the larger number of substances are either liquid or solid, and incapable of passing into the gaseous state, even at very high temperatures, the importance of discovering the law which governs the volumes of these forms of matter, has long been recognised, and for some time past has much engaged the attention of philosophers.

The first chemist who drew attention to this subject was Dr. Thomson, who published a Table*, in the year 1831, of the specific volumes of certain of the metals, obtained by dividing their atomic weights by their specific gravities. In this table a remarkable coincidence of volume is observed in several of the metals most nearly allied in chemical characters.

More recently the subject has been examined in detail by Kopp, Schröder and Persoz, whose researches have thrown considerable light on this obscure department of physics.

Kopp† drew attention to the circumstance, that in many cases isomorphous bodies possess the same atomic volume, the law being correct when the isomorphism is strictly accurate, but approximating only when this is not the case. He admits also that perfect equality of the volume exists only at particular temperatures, on account of the unequal expansion of isomorphous crystals.

Schröder‡ made the interesting observation, that the remainder is the same when the primitive volume of the corresponding member of a series of analogous compounds is subtracted from them; thus AO, BO and CO leave a constant remainder when the known volumes of A, B and C are subtracted respectively from the known atomic volumes of the compounds.

Kopp§ confirms this discovery to a certain extent, believing, however, that the primitive volumes A, B and C must be assumed in certain classes of salts to be different when in combination with O from their volumes when isolated. He also announces the discovery‖ of a great regularity in the physical properties of analogous organic compounds, so much so, that the study of the physical characters of the compounds of one body enables us to predicate those of the corresponding compounds of another substance.

The discoveries of Schröder and Kopp, with regard to

* Chemistry of Inorganic Bodies, vol. i. p. 14.

† Poggendorff's *Annalen*, Band xlvii.; and *Annalen der Chemie*, Band xxxvi. S. 1.

‡ Poggendorff's *Annalen*, Band l. S. 554.

§ *Ueber das Specifische Gewicht der Chemischen Verbindungen.* Frankfort, 1841.

‖ *Annalen der Chemie*, Band xli. S. 79.

the atomic volumes of liquid and solid bodies, do not, except in a very few instances, indicate an approach to a simple multiple ratio of volumes, and are therefore only in a small degree connected with the law of gaseous volume. We therefore thought it desirable to enter into a series of inquiries on this most important subject, and we have now the honour to lay before the Society the First Part of these researches.

Hitherto the inquiry has been principally confined to solid bodies, on the just ground that their diminished rate of expansion offers less difficulty to the discovery of the law regulating volumes. But there is an objection to the use of solids, which to a certain extent counterbalances this advantage, viz. that they do not present matter in a perfectly uniform condition, free from cohesion. On consideration, therefore, we were led to believe this objection to be so powerful, that we conceived it to be preferable, so to separate the particles of the body under examination, as to destroy their cohesion, without at the same time altering their chemical properties. Solution in water was the obvious means of effecting this purpose, according to the notions generally entertained of solution, and it was therefore resolved to experiment principally upon soluble bodies of well-known and defined constitution. At the same time, it was necessary to examine the relation of the solid volume to the volume of the body when in solution, so as to indicate the connection between the solid and the liquid atom.

The specific gravities of salts are little known, and even when recorded are described so differently by different observers, that it was necessary to determine the specific gravity in each of the cases upon which the experiments were instituted. Hitherto the volumes of solids had always been referred to an equal volume of water; in other words, the *solid* form of matter had been referred to its *liquid* form. This difference of conditions was no small impediment to the discovery of a law which might be modified for each form of matter*. By determining the volume of the substance in solution, we compared it in its liquid state to the liquid form of matter in

* Before leaving the notice of the labours of those who have preceded us in inquiring into the nature of specific gravity, we must not omit to notice the speculations of the ingenious Persoz, who (in vol. xl. of the *Ann. de Ch. et de Phys.*, p. 119) drew attention to the equality in volume of isomorphous bodies, and even of some which were not isomorphous. Persoz also believes that the volumes of all bodies are multiples of 56, or half the atomic weight of water; but this idea does not agree with recorded observations, and is directly contradicted by accurate estimations of specific gravities.—See the work of M. Persoz, *Introduction à l'Etude de la Chimie Moléculaire*, page 834 *et seq.*

which it was dissolved; and by contrasting the volume of the solids with each other, and also with their volume when rendered liquid by water, we conceived that we might be placed in more favourable conditions for elucidating a law.

Bishop Watson* was the first chemist who endeavoured to estimate the increase of volume when salts dissolve in water; for, although both Gassendus† and the Abbé Nollet‡ had written, and Ellis§ had experimented upon the same subject, they had arrived at conclusions entirely erroneous, which were removed by Watson's more accurate experiments. Watson's apparatus was rude enough, being a matrass capable of holding 67 ounces of water, into which he projected 24 pennyweights of each of the salts upon which he experimented, and noted the rise in the neck of the matrass. He completely exploded, however, the idea that saline substances dissolve in water without increasing its bulk.

Between the time of Bishop Watson, whose investigations on this subject are most profound, when we consider the period at which he wrote, and that of Dalton, there were no labourers in this field to whom we need draw especial attention. In the year 1840, Dalton‖ made the interesting discovery, that sugar and certain salts on being dissolved in water increase its bulk only by the amount of water pre-existing in them. He generalized this observation by asserting that all hydrated salts dissolve in water, increasing its bulk merely by their amount of water of hydration, while anhydrous salts do not at all increase the bulk of the water in which they are dissolved.

But it must not be forgotten, that when Dalton published this paper, he was much enfeebled by illness, and on this account it does not derogate from the acuteness of the philosopher, that Mr. Holker was unable to confirm Dalton's results in repeating the experiments in 1843**. He did so, however, in the case of sulphate of magnesia, and approximatively in that of one or two other salts. As Mr. Holker's paper has not been published, we are unable to state his claims in the progress of this subject; but we believe that an attempt was made to show a multiple relation in the increments of *isomorphous* salts, although his experiments were conducted

* Philosophical Transactions, 1770.

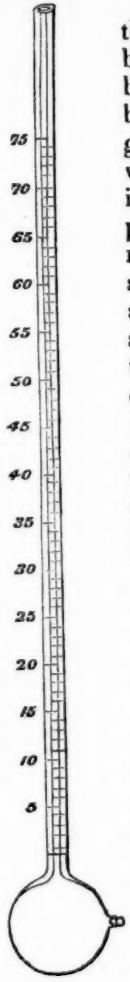
† *Gass. Phys.* lib. i. sect. 1. cap. 3.

‡ *Leçons de Physique*, vol. iv. § Berlin Memoirs, 1750.

‖ "On the quantity of Acids, Bases and Waters in Salts, and a new mode of measuring them," read to the Manchester Literary and Philosophical Society, 6th October 1840, and published as a pamphlet.

** Paper read to the Manchester Literary and Philosophical Society, but not published.

without reference to the density or temperature of the solution on which he operated.



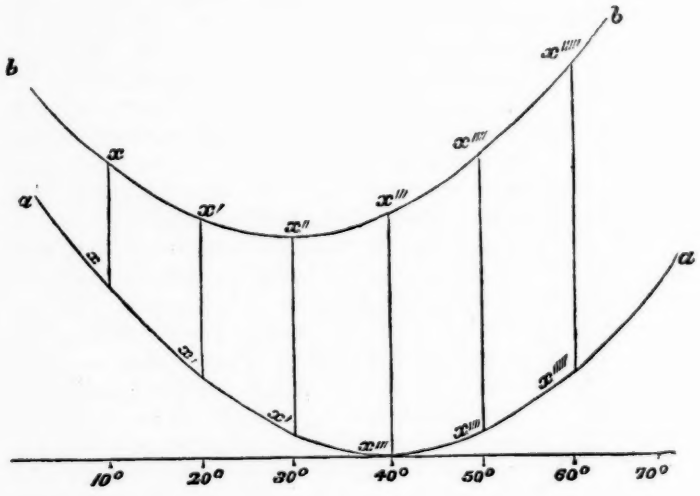
Volumenometer for Salts in Solution.
One-half the size of the Instrument, used with 1000 grains of water.

In the experiments about to be described, the apparatus for estimating the volume of bodies when dissolved, consisted of a glass bulb, to which a stem was attached. The bulbs varied in capacity from 1000 to 4000 grains of water, and the diameter of the stem was from one-eighth to one-sixteenth of an inch, according to the character of the experiment. In the bulbs employed for ordinary purposes, each grain of water occupied about a quarter of an inch in the stem, and as the graduation was made in grains of water at 60°, the experiment could be made to the tenth of a grain of increase in volume. In every case care was taken that the salts used were rigidly pure, and in their proper state of hydration. The distilled water employed to dissolve them was deprived of air by long-continued boiling, and preserved for use in stoppered bottles. The salt was introduced by a tubulure in the side of the bulb in the following manner. The bulb was filled with water until it reached a fixed point in the stem, when it was reclined and the stopper removed. A weighed quantity of salt was then introduced by a dry funnel, and the stopper reinserted, care being taken that no air was admitted during the operation; the increase in the stem, after the salt was dissolved, gave the volume of the quantity of salt used in the experiment. It was found by repeated trials that no loss of volume or error was occasioned by the moistening of the tube during the time it was in the reclining posture, for the precaution was always taken to moisten the walls of the tube previous to the experiment. It is evident that the volume occupied by a salt in solution must be modified by the position of the point of its maximum density. Despretz has shown* that the temperature at which solutions are most dense becomes lower in proportion to the quantity of matter held in solution. It is also known, from the experiments of Dalton and others, that from the point of maximum density to about 30° above or below it,

* *Annales de Chimie*, tome lxx. an. 1839, p. 81.

water and dilute solutions expand according to the square of the temperature from that of greatest density. From Despretz's table of the expansion of water, it appears that the law is not true as far as 212°. As far however as it does hold good, it is evident, from the properties of the parabola, that the volume occupied by a salt in solution will increase in arithmetical progression with the temperature at which the experiment is made.

For instance, let *a a* in the following diagram be a parabola representing the expansion of water, and let *b b* be a similar parabola representing the expansion of a solution. Let the latter parabola have its vertex or point of greatest density opposite 30°, while the former parabola has its vertex at 40°; then $x\,x$, $x'\,x'$, $x''\,x''$, &c., quantities which increase in arithmetical progression, will represent the volumes occupied by the salt in solution at the temperature of 10°, 20°, 30°, &c.



In a similar manner it may be shown that the volume occupied by each equivalent of a salt in solution at any given temperature will increase with the density of the solution. In order to ascertain the amount of influence exercised by a change in the position of the point of maximum density, we have made a series of experiments on the expansion of water and of solutions by heat, which we propose to lay before the Society in a succeeding memoir. In order, however, to render evident the augmentation of volume caused by increased density, we have constructed the following table of the volumes

occupied by 172 grains, or one equivalent of sugar, in solutions of different degrees of density.

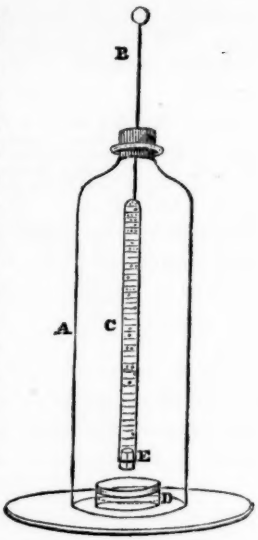
TABLE I.

Ratio of the quantity of sugar to the quantity of water in which it was dissolved.	Temperature.	Volume in grain measures of water.
1 : 120	60°	99·00
1 : 10	52	105·09
1 : 1	52	107·01
3 : 1	52	108·06

As the rate of expansion of dilute solutions is so near that of water, it was in most cases sufficient, for a very close approximation to absolute accuracy, to take the observation within a few degrees below 60°, the temperature of the graduation of our volumenometers. Whether this temperature of graduation is the best to adopt, is a point which we shall have to discuss in our future communications; but at present it may be sufficient to state that its convenience was considerable, as being the average temperature of our laboratories. In all cases, then, in the following experiments, unless where it is otherwise stated, the temperature of the solution was about 60°, which was also, of course, the temperature of the water before the salt was introduced. In the case of the sulphates of the magnesian class of metals, the temperature chosen was higher than 60°, in order to make up for a diminished rate of expansion, owing to a greater degree of dilution in the solution.

The specific gravity of the salts was determined in an equally simple manner. A saturated solution of the salt about to be experimented upon (made by dissolving an excess of the salt by heat and allowing the solution to cool) was placed in the apparatus already described, and a weighed portion of the salt was then introduced, care being taken that the temperature did not vary during the experiment. As the new portion of salt could not dissolve, the increase in the stem indicated the volume due to the quantity of salt introduced, and afforded data for calculating the specific gravity. In many cases oil of turpentine was used instead of the saline solution.

It was frequently desirable, especially in the case of hydrated salts rendered anhydrous, to avoid the use of water, and in the case of organic compounds, also of turpentine; and to meet such cases we constructed the following simple apparatus, which we believe to possess various advantages.



A is the receiver of an air-pump, furnished at the top with a collar and sliding rod. B C is a small graduated tube filled with the substance, the volume of which is to be determined; it is closed with a stopper E, perforated with a hole of dimensions so small as to prevent any of the salt from falling out. D is a cup of mercury placed immediately below the graduated tube C. The sketch indicates the position of the apparatus on an air-pump when the experiment is about to be performed. The receiver is then exhausted as thoroughly as possible, and the indication of the siphon-gauge is accurately noted. The graduated tube is then lowered by means of the sliding rod until it touches the bottom of the cup containing the mercury, which, after the admission of air, flows into the tube until it is filled. The whole contents of the tube are then thrown into water, and the salt is washed away by decantation. The mercury is dried by bibulous paper, and restored to the tube. If the temperature be different from that which it possessed in the first part of the experiment, it is restored to the original temperature, or a correction is made for the difference. It is now obvious that the space in the tube unoccupied by the mercury is that which was formerly filled with the salt. To this, however, must be added a slight correction for the imperfect nature of the vacuum, which is not Torricellian,—a correction which need not exceed $\frac{1}{200}$th of the volume observed. With these preliminary descriptions and observations, we now proceed to describe the details of our experiments, throwing them into various classified groups of salts, for the purpose of easy reference.

The first group described is remarkable for containing a large amount of water of hydration.

Sulphate of Copper, $CuO, SO_3 + 5HO = 124{\cdot}88$.—The third part of an equivalent of this salt, 41·62 grains, dissolved in 3140 grains of water at 32°, with an increase of 13·15, but dissolved in water at 90°, with an increase of 15·0.

$CuO, SO_3 + 5HO$, vol. in solution 45·0.

Half an equivalent of this salt, 62·44 grains, being immersed in a saturated solution, occupied the volume of 27·7 water-grain measures.

	Sp. vol.		Sp. gr.
$CuO, SO_3 + 5HO$, vol. of salt	55·4	...	2·254

Kopp found for the specific gravity of this salt the number 2·274.

Sulphate of Alumina, $Al_2O_3, 3SO_3 + 18HO = 333·7$.—The salt used in the experiments was carefully prepared, and obtained in tolerably good crystals. The eighth part of an equivalent, 41·7 grains, dissolved in 1000 of water, with an increase of 20·0 in one experiment, and 19·9 in another, the temperature of observation being 51°.

I.	Sulphate of alumina, vol. in solution	160·0
II.	... ...	159·2
	Mean . .	159·6

The same quantity of salt thrown into turpentine caused in two experiments an increase of 25·0, and in a third of 24·9.

				Sp. gr.
I.	Sulphate alumina, vol. of salt	200·0	...	1·668
II.	... ...	199·2	...	1·675
	Mean . .	199·6	...	1·671

Sulphate of Soda, $NaO, SO_3 + 10HO = 161·48$.—Sulphate of soda, crystallized out of a strong warm solution, carries down 10 atoms of water. Of this salt, about one-fourth of an equivalent (40·4 grains), on being dissolved in 1000 grains of water, caused in two experiments an increase of 23·0, at a temperature of 59°; and in a third experiment of 22·8 at the same temperature.

I. II.	$NaO, SO_3 + 10HO$, vol. in solution =	91·8
III.	... ...	91·2
	Mean . .	91·5

The same quantity of the salt being immersed in a saturated solution occasioned an increase of 27·8; and on a second experiment, of 27·2 at a temperature of 62°.

				Sp. gr.
I.	$NaO, SO_3 + 10HO$, vol. of salt	111·1	...	1·453
II.	... ...	108·7	...	1·485
	Mean . .	109·9	...	1·469

When sulphate of soda crystallizes from a weak cold solution, it carries down a quantity of water, corresponding to eleven equivalents. In two experiments, the volume in solution of salt procured in this way was 98; but we apprehend that the water is merely mechanical, for reasons which will be seen hereafter, as the volume of the salt itself, by a mean of several experiments, came out to 119·5, whereas had this

eleventh atom of water been combined it should have been 121.

Biborate of Soda, $NaO, 2BO_3 + 10HO = 191{\cdot}23$.—On dissolving 40 grains of this salt in 1000 of water, the increase was 19·2 at a temperature of 55°.

$NaO, 2BO_3 + 10HO$, vol. in solution 91·7.

Half an equivalent, or 95·61 grains, on being placed in a saturated solution, occasioned an increase of 55·5; and 47·8 grains caused an increase of 27·5; both experiments being made at a temperature of 55°.

			Sp. gr.
I.	$NaO, 2BO_3 + 10HO$, vol. of salt	111 ...	1·722
II.	... ...	110 ...	1·738
	Mean . .	110·5 ...	1·730

Chloride of Strontium, $Sr, Cl + 6HO = 133{\cdot}32$.—There are two hydrates of chloride of strontium, the one with nine, and the other with six equivalents of water. To determine which of these hydrates was under examination, 4·324 grammes were heated to redness with a loss of 1·75 gramme = 40·47 per cent., showing that the hydrate was that with six equivalents of water, which gives by calculation 40·50 per cent.

On dissolving 40 grains of this salt in 1000 of water, the increase occasioned at a temperature of 56° was 16·0; a second experiment, in which the same quantities were used, gave exactly the same result.

I. II. $Sr Cl + 6HO$, vol. in solution 53·3.

The same quantity of salt (40 grains), immersed in a saturated solution, caused an increase of 20·0 at a temperature of 57°; and on a second experiment of 19·7.

			Sp. gr.
I.	$Sr Cl + 6HO$, vol. of salt	66·6 ...	2·000
II.	... ...	65·6 ...	2·030
	Mean . .	66·1 ...	2·015

Chloride of Calcium, $Ca Cl + 6HO = 109{\cdot}92$.—On dissolving 55 grains, or the half of an equivalent of this salt, in 1000 grains of water, an increase of 28·0 was obtained at the temperature of 70°; and in a second experiment 27·6 at 60°.

I.	$Ca Cl + 6HO$, vol. in solution	56·0
II.	... ...	55·2
	Mean . .	55·6

The same quantity of salt thrown into turpentine caused an increase of 32·7 and 32·8 in two experiments.

			Sp. gr.
I.	$Ca Cl + 6HO$, vol. of salt	65·4 ...	1·682
II.	... ...	65·6 ...	1·677
	Mean . .	65·5 ...	1·680

Chloride of Magnesium, Mg Cl + 6HO = 102·16.—Millon has lately described this salt as containing $6\frac{1}{2}$ atoms of water; but, as we have not been successful enough to obtain this hydrate, we retain the old formula. 25·54 grains, or the fourth of an equivalent, dissolved in 1000 grains of water at 53°, with an increase of 14·0.

Mg Cl + 6HO, vol. in solution = 56·0.

The same quantity, 25·54 grains, gave, in four experiments, respectively, 16·5; 16·0; 16·4; 16·5.

			Sp. gr.
I.	Mg Cl + 6HO volume of salt	66·0 ...	1·548
II.	... ...	64·0 ...	1·595
III.	... ...	65·6 ...	1·557
IV.	... ...	66·0 ...	1·548
	Mean . .	65·4 ...	1·562

The salts now examined are not calculated, on account of the deliquescent character of several of them, to produce absolutely accurate experimental results; but, notwithstanding this circumstance, the determination of their volumes is sufficiently uniform to indicate the theory. The actual volume observed for each of the salts in solution, when divided by 9, the atomic volume of water, yields as the quotient the same number as that representing the atoms of water in the salt. Hence it is quite certain that the salts now described dissolve in water without adding to its bulk more than is due to the liquefaction of the water in chemical combination with them.

The volumes of the salts in their solid state possess a number considerably higher than that representing the liquid volume, but affect a divisor, which is the same for all the salts, allowing for errors of experiments, or for alterations caused by incidental circumstances. This divisor is a number either equal or approximating to 11. When the volumes of the salts in the solid state are divided by this number, the quotient represents the number of atoms of water attached to the salt. The most natural view of this circumstance is to suppose that water in combination as a solid with a salt possesses a higher volume than liquid water, just as in the case of ice. If this view be correct, the atomic volume of the salts described is the same in the state of a solid as when in solution, the only difference being, that in the one case the volume is expressed by liquid, in the other by solid water. In this case, however, water in combination with a salt does not possess the same volume as ice, which, according to our experiments, detailed in another part of this paper, has a volume of 9·8, and not of a number approaching to 11.

Yet there is nothing extravagant in the idea that water combined with a salt may have a volume different from that of ice. Indeed, we are inclined to be of the opinion that ice itself represents nearly the mean of the volume of water uncombined and that of combined water. Be this as it may, it will be observed, as we proceed, that the number 11 is the best exponent of one class of our experiments on specific gravity; and therefore, without resting its claims to acceptance entirely on the present experiments, we assume it in the following tables as the theoretical result for each class of salts. With these views we tabulate the experiments which have been already detailed.

TABLE II.—Showing the volumes occupied by certain salts containing a large amount of hydrate water.

Designation.			Volume in solution.			Volume as salt.				
Name.	Formula.	Atomic Weight.	Volume in solution.	9, or volume of water as unity.	Volume by calculation.	Volume of salt by experiment.	11, an assumed number as unity.	Volume by calculation.	Specific gravity by calculation.	Specific gravity by experiment.
Sulphate of copper.....	CuO, SO_3+5HO	124·88	45·	5	45	55·4	5	55	2·270	2·254
Sulphate of alumina	$Al_2O_3, 3SO_3+18HO$	333·7	159·6	18	162	199·6	18	198	1·685	1·671
Sulphate of soda.....	NaO, SO_3+10HO	161·48	91·6	10	90	109·9	10	110	1·468	1·469
Biborate of soda	$NaO, 2BO_3+10HO$	191·23	91·7	10	90	110·5	10	110	1·738	1·730
Chloride of strontium .	$SrCl+6HO$	133·33	53·3	6	54	66·1	6	66	2·020	2·015
Chloride of calcium	$CaCl+6HO$	109·92	55·6	6	54	65·5	6	66	1·665	1·680
Chloride of magnesium.	$MgCl+6HO$	102·16	56·0	6	54	65·4	6	66	1·548	1·562

There are some salts which do not take up any space in solution, except that due to their water, but which assume a volume due to one of their constituents on becoming solid; the potash and ammonia alums are examples of this class.

Sulphate of Alumina and Potash, $Al_2O_3\,3SO_3 + KO\,SO_3 + 24HO = 474·95$.—59 grains of alum dissolved in 1000 grains of water, gave the increase of 27·0 in one experiment and 27·1 in another, both at the temperature of 60°.

I.	Alum, volume in solution	217·3
II.	... ...	218·1
	Mean . .	217·7

On throwing 59·37 grains into a saturated solution, an increase of 34·4 was obtained in the first experiment; of 34·7 in a second; of 34·3 in a third; and of 34·2 in a fourth, all at a temperature about 60°.

			Sp. gr.
I.	Alum, vol. of salt	275·2 ...	1·726
II.	... ...	277·6 ...	1·711
III.	... ...	274·4 ...	1·730
IV.	... ...	273·6 ...	1·735
	Mean . .	275·2 ...	1·726

Sulphate of Alumina and Ammonia, Al_2O_3, $3SO_3 + NH_4O$, $SO_3 + 24HO$ = 454·26.—20 grains of this salt dissolved in 4100 grains of water with an increase of 10·0 at 58°.

Ammoniacal alum, vol. in solution 227·1

The eighth part of an equivalent, 56·78 grains, immersed in turpentine, caused a rise in the stem of 34·9 in one experiment and 35·0 in another, the temperature being 60°.

			Sp. gr.
I.	Ammonia alum, vol. of salt	279·2 ...	1 627
II.	... ...	280·0 ...	1·623
	Mean . .	279·6 ...	1·625

Chrome Alum, Cr_2O_3, $3SO_3 + KO$, $SO_3 + 24HO$ = 504·1. —On dissolving 32 grains of this salt in 4100 grains of water, an increase of 13·7 was effected at 37°.

Chrome alum, vol. in solution 215·8

In two experiments 63 grains of this salt thrown into turpentine caused an increase of 34·5.

		Sp. gr.
Chrome alum, volume of salt	276 ...	1·826

Iron Ammonia-alum, Fe_2O_3, $3SO_3 + NH_4O$, $SO_3 + 24HO$ =481·03.—On dissolving 30·06 grains in 1000 grains of water, an increase of 14·3 was obtained at a temperature of 37°.

Iron alum, vol. in solution 228

The eighth part of an equivalent, 60·13 grains, produced an increase of 35·0 measures when thrown into turpentine.

		Sp. gr.
Ammoniacal iron alum, vol. of salt	280·0 ...	1·718

Pyrophosphate of Soda, $2NaO, PO_5 + 10HO$ = 224·15.—The eighth part of an equivalent of the crystallized pyrophosphate, 28 grains, dissolved in 1000 grains of water with an increase of 11·2 in one experiment and of 11·3 in another, the temperature in both cases being 58°.

Pyrophosphate of soda, vol. in solution 89·6
... ... 90·4
Mean . . 90·0

On immersing 56·04 grains of the salt in a saturated solution, an increase of 30·5 was obtained in two experiments.

Sp. gr.
Pyrophosphate of soda, vol. of salt 122·0 ... 1·836

By tabulating the results thus obtained we find the following relationship between the class of alums.

TABLE III.—Showing the volumes of certain Alums*.

Designation.			Volume in solution.			Volume in state of salt.				
Name.	Formula.	Atomic weight.	Vol. in solution by experiment.	9, or vol. of water as unity.	Vol. by theory.	Vol. of salt by experiment.	11, taken as unity.	Vol. of salt by theory.	Specific gravity by theory.	Specific gravity by experiment.
Potash alum ...	$Al_2O_3,3SO_3,KO,SO_3+24HO$	474·95	217·7	24	216	275·2	25	275	1·727	1·726
Ammonia alum.	$Al_2O_3,3SO_3+NH_4O\ SO_3+24HO$	454·26	227·1	25	225	279·6	25	275	1·652	1·625
Chrome alum...	$Cr_2O_3,3SO_3+KO,\ SO_3+24HO$	504·1	215·8	24	216	276·0	25	275	1·833	1·826
Iron alum ...	$Fe_2O_3,3SO_3+NH_4O,\ SO_3+24HO$	481·03	228	25	225	280·0	25	275	1·749	1·718
Pyrophosphate of Soda ...	$2NaO,PO_5+10HO$	224·15	90	10	90	122	11	121	1·852	1·836

The peculiarity of the salts described in the above table is, that the quotient of the divisor for the potash alums in the solid state is not the same as in the state of solution, and that the ammoniacal alums possess one volume in solution greater than the corresponding potash alums, both of which peculiarities will find an explanation as we proceed. Pyrophosphate of soda shares this peculiarity, and is therefore introduced into the table.

We now proceed to describe a class of hydrated salts, in which the divisor for the solid volume is certainly not the number 11.

Carbonate of Soda, $NaO,\ CO_2+10HO=143·4$.—On dissolving 35·85 grains of this salt in 1000 grains of water, the increase was 22·5 in one experiment at 64°, and 22·9 in a second experiment at 65°.

I. $NaO,\ CO_2+10HO$, vol. in solution 90·0
II. ... ... 91·6
Mean . . 90·8

* *Vide* conclusion for explanation of the high volume of ammonia alums.

On throwing 35·8 grains of the salt into turpentine, the increase was 24·7, 24·5, 24·6, and 24·8 in consecutive experiments with different specimens.

			Sp. gr.
I.	Carbonate of soda, vol. of salt	98·8 ...	1·451
II.	... ...	98·0 ...	1·463
III.	... ...	98·4 ...	1·457
IV.	... ...	99·2 ...	1·446
	Mean . .	98·6 ...	1·454

Rhombic Phosphate of Soda, $2\,NaO\,HO,\,PO_5 + 24HO = 359·1$.—The eighth part of an equivalent of this salt, 44·9 grains, dissolved in 1000 grains of water with an increase of 27·0 in one experiment, and 27·1 in a second; by some mistake the temperature of the solution has not been recorded.

I.	Phosphate of soda, vol. in solution	216·0
II.	... ...	216·8
	Mean . .	216·4

The same quantity of salt thrown into turpentine caused an increase of 29·4 in two experiments, and 29·5 in a third.

			Sp. gr.
I.	Phosphate of soda, vol. of salt	235·2 ...	1·527
II.	... ...	235·2 ...	1·527
III.	... ...	236·0 ...	1·521
	Mean . .	235·5 ...	1·525

Sub-phosphate of Soda, $3NaO,\,PO_5 + 24HO = 381·6$.—The eighth part of an equivalent of this salt, 47·7 grains, dissolved in 1000 grains of water, with an increase of 27·1 in two experiments at 48°.

I. II. Sub-phosphate of soda, vol. in solution 216·8

The same quantity of salt thrown into turpentine produced an increase of 29·4 in two experiments under favourable circumstances, although in another experiment, in which we were not satisfied with the state of hydration of the salt, the increase was only 28·9.

Sub-phosphate of soda 235·2 ... 1·622

Arseniate of Soda, $2NaO,\,HO,\,AsO_5 + 24HO = 402·9$.—On dissolving 50·36 grains, the eighth part of an equivalent, in 1000 grains of water, an increase of 27·2 was obtained at a temperature of 54°.

Arseniate of soda, vol. in solution 217·6

The same quantity of salt thrown into a saturated solution caused an increase of 29·0 in several experiments. This salt

loses its water with such facility that it is almost impossible to obtain it in a state well-fitted for experiment. In two specimens of salts, prepared at different times, the volume for the above quantity of salt was 29·7 and 29·8; but as in most cases it was only 29·0, we give the result most generally obtained.

Arseniate of soda, vol. of salt 232·0 ... 1·736

Sub-arseniate of Soda, $3\,NaO,\,AsO_5 + 24\,HO = 425{\cdot}2$.—The eighth part of an equivalent, 53·15 grains, of this salt dissolved in 1000 grains of water, with an increase of 27·0 in one experiment, and 26·9 in another, at a temperature about 55°.

I.	Sub-arseniate of soda	216·0
II.	... ...	215·2
	Mean . .	215·6

The same quantity of salt immersed in turpentine caused an increase of 29·4 and 29·5 in two experiments.

I.	Sub-arseniate of soda, vol. of salt	235·2	1·808
II.	... ...	236·0	1·801
	Mean . .	235·6	1·804

Cane-Sugar, $C_{12}\,H_{11}\,O_{11} = 171{\cdot}60$.—25·8 grains of sugar dissolved in 3140 grains of water caused an increase of 14·8 at 32°; 42·9 grains, or the fourth of an equivalent, gave an increase of 25·0 at 60° in two experiments.

I.	Cane-sugar, vol. in solution	98·4
II.	... ...	100·0
III.	... ...	100·0
	Mean . .	99·5

300 grains of sugar-candy thrown into alcohol previously saturated with it, caused an increase in the first experiment of 188·0, in the second of 188·75; in a third experiment, 49·65 grains thrown into turpentine caused an increase of 31·0; and the same quantity, in a fourth experiment, of 31·1, the temperature in all the cases being about 60°.

			Sp. gr.
I.	Cane-sugar, vol. of solid	107·5 ...	1·596
II.	... ...	107·9 ...	1·590
III.	... ...	107·1 ...	1·602
IV.	... ...	107·5 ...	1·596
	Mean . .	107·5 ...	1·596

In this section a class of salts presents itself, in which the volumes are clearly not represented by any multiple of 11; yet they are uniform in their isomorphous relations, and are sensibly multiples of the same number. To discover whether

the solid volume have any relation to that occupied by ice, we have determined the specific gravity of the latter with great care. The distilled water, which we converted into ice, was deprived of air by long-continued boiling, and a weighed portion of the ice was quickly immersed in water at 32°, the balance being kept at the same temperature during the weighing of the ice. The rise in the stem of the volumenometer, in which fragments of ice had previously been placed, indicated the volume due to the quantity of ice immersed. On treating in this manner 54·2 grains of ice, a rise in the stem of 59·0 was produced; and in a second experiment 52·8 grains of ice occasioned an increase of 57·5, the temperature in both cases being exactly 32°.

	Specific volume.		Specific gravity.
I. Ice volume	9·797	...	0·9186
II.	9·801	...	0·9183
Mean . .	9·799	...	0·9184

As the true specific gravity of ice is a subject of much importance, we place here all the recorded results, as given in Bottger's most useful work on specific gravity, and in the first volume of Scoresby's Arctic Regions.

Specific gravity of ice	0·888	Dulk.
... ...	0·937	Irvine.
... ...	0·945	Williams.
... ...	0·885	Meineke.
... ...	0·905	Heinrich Kraft.
... ...	0·927	Osann.
... ...	0·950	Roger and Dumas.
... ...	0·920	Scoresby.
Mean . .	0·919	

The mean of all these experiments, differing only $\frac{1}{1000}$ from our own determination, warrants us in concluding that our result is accurate, and that 9·80 may safely be taken as the specific volume of an atom of ice. Now it must at once strike the observer of the previous experiments, that this number forms the divisor for the volumes of the salts described in the present section.

TABLE IV.—Showing the volumes occupied by certain Phosphates, Arseniates, Carbonate of Soda and Cane-sugar.

Designation.			Volume in solution.			Volume of salt.				
Name.	Formula.	Atomic weight.	Volume in solution by experiment.	9, or volume of water as unity.	Volume by theory.	Volume of salt by experiment.	9·8, or volume of ice as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Carbonate of soda	$NaO, CO_2 + 10HO$	143·4	90·8	10	90	98·6	10	98·0	1·463	1·454
Phosphate of soda	$\{2NaO, HO, PO_5 + 24HO\}$	359·1	216·4	24	216	235·5	24	235·2	1·527	1·525
Sub-phosphate of soda	$3NaO, PO_5 + 24HO$	381·6	216·8	24	216	235·2	24	235·2	1·622	1·622
Arseniate of soda	$\{HO, 2NaO, AsO_5 + 24HO\}$	402·9	217·6	24	216	232·0	24	235·2	1·713	1·736
Sub-arseniate of soda	$3NaO, AsO_5 + 24HO$	425·2	215·6	24	216	235·6	24	235·2	1·808	1·804
Cane-sugar	$C_{12} H_{11} O_{11}$	171·6	99·5	11	99	107·5	11	107·8	1·591	1·596

Connected with the latter group, there is a class of salts which come out uniformly with themselves, but the divisor of which is not 11 in the solid state. We subjoin them in the following group.

Sulphate of Magnesia, $MgO, SO_3 + 7HO = 123{\cdot}86$.—When this salt is dissolved in a large quantity of cold water, the volume observed after solution is always less at ordinary temperatures than that due to the water contained in the salt. That this diminution is due to a contraction caused by an affinity of the salt for water is shown by the fact, that anhydrous sulphate of magnesia dissolved in a large quantity of water actually lessens, instead of increasing the bulk of the water; and to compensate for this contraction, a certain temperature has to be given to the water. In the following experiments with the sulphates of magnesia, zinc and iron, this circumstance has been attended to, and the temperature is given at which the results come out exact.

31 grains of crystallized sulphate of magnesia were dissolved in 3140 grains of water at 32°, and caused an increase of 15·22; at 85° the increase was 15·75.

$MgO, SO_3 + 7HO$, vol. in solution 63.

Half an equivalent, 61·93 grains, being placed in a saturated solution of the salt, caused an increase of 37·5 in one experiment, but in three other experiments the increase was not greater than 37·2; the temperature in all the cases being 54°.

			Sp. gr.
I. $MgO, SO_3 + 7HO$, vol. of salt	75·0	...	1·651
II.	74·4	...	1·664
III.	74·4	...	1·664
IV.	74·4	...	1·664
Mean . .	74·55	...	1·660

Sulphate of Zinc, $ZnO, SO_3 + 7HO = 143·43$.—This salt possesses the same property as sulphate of magnesia, of causing a contraction when the anhydrous salt is dissolved in a large quantity of cold water.

35·9 grains were dissolved in 3140 grains of water at a temperature of 32°, causing a rise in the stem of 14·03. At 90° the rise was 15·77.

$ZnO, SO_3 + 7HO$, vol. in solution 63.

The half of an equivalent of this salt, 71·71 grains, being thrown into a saturated solution, caused an increase of 37·1; and 35·85 grains produced a rise in the stem of 18·6 in two experiments, and of 18·5 in a fourth.

			Sp. gr.
I. $ZnO, SO_3 + 7HO$, vol. of salt	74·2	...	1·933
II.	74·4	...	1·928
III.	74·4	...	1·928
IV.	74·0	...	1·937
Mean . .	74·25	...	1·931

Sulphate of Iron, $FeO, SO_3 + 7HO = 138·3$.—The fourth part of an equivalent, 34·6 grains, dissolved in 3140 grains of water at 32° with an increase of 15·25, which became 15·75 at 80°.

$FeO, SO_3 + 7HO$, vol. in solution 63.

The same quantity of salt thrown into turpentine gave in one experiment an increase of 18·6, in another of 18·7, and in a third of 18·6.

			Sp. gr.
I. $FeO, SO_3 + 7HO$, vol. of salt	74·4	...	1·860
II.	74·8	...	1·850
III.	74·4	...	1·860
Mean . .	74·5	...	1·857

Sulphate of Nickel, $NiO, SO_3 + 6HO = 131·74$.—This salt we found to contain only 6 atoms of water instead of 7 atoms, as usually described; but it is known to crystallize with both proportions. On dissolving 35 grains in 1000 of water, the increase obtained was 14·0 at a temperature of 55°.

$NiO, SO_3 + 6HO$ = vol. in solution 52·7.

We have not ourselves obtained the specific gravity of this

salt, but this has been determined by Kopp, who gives it at 2·037, without however describing the character of the hydrate which he examined. It is possible, therefore, that it may not be the same as that which we have examined; but presuming it to be so, the volume of this salt, according to Kopp, would be

		Sp. gr.
$NiO, SO_3 + 6HO$, vol. of salt	64·6 ...	2·037.

The volumes of the magnesian sulphates with 7 atoms of water are obviously less than those which would result were they multiples of the volume 11. But as we have already seen that the water of hydration does not always enter into combination with the volume 11, but occasionally with that of 9·8, or the volume of ice, the results obtained may be explained on this view. Graham*, in his researches on the phosphates, and on the heat of combination, drew attention to the fact, that the atoms of water seem to be attached together in *twos*. Millon† more lately has shown that the two last atoms of water in sulphate of magnesia are less firmly attached than the five remaining atoms; that a magnesian sulphate in fact may be viewed as

$$MgO, SO_3 + 5HO + 2HO.$$

That 5 atoms of water form the natural numbers for the magnesian sulphates we have evidence in the salts of copper and manganese, both of which possess these 5 atoms of water in combination with a volume of 11, at least.

$CuO, SO_3 + 5HO$ vol. of salt	55·4	(P. and J.)
$MnO, SO_3 + 5HO$ ...	57·6	(Kopp.)

As then the two additional atoms of water are retained by a less feeble affinity than the remaining five, may we not assume that they are present, as in the case of other salts possessing a feeble affinity for water, with the volume of ice, whilst the original 5 atoms possess the higher volume of 11? The following table will show that this hypothesis gives results by calculation which do not differ widely from those obtained by experiment.

* Phil. Trans., part 1. 1837, page 67.

† *Annales de Chimie*, 3 série, t. xii. p. 134.

TABLE V.

Designation.			Volume in solution.			Volume of salt.				
Name.	Formula.	Atomic Weight.	Volume in solution.	9, or volume of water as unity.	Volume by theory.	Volume of salt by experiment.	11 as unity for 5 atoms, and the volume of ice for 2 atoms.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Sulphate of magnesia	$MgO, SO_3+5HO+2HO$	123·86	63	7	63	74·55	5+2	74·6	1·660	1·660
Sulphate of zinc	$ZnO, SO_3+5HO+2HO$	143·43	63	7	63	74·25	5+2	74·6	1·926	1·931
Sulphate of iron	$FeO, SO_3+5HO+2HO$	138·3	63	7	63	74·5	5+2	74·6	1·854	1·857
Sulphate of nickel ...	$NiO, SO_3+5HO+HO$	131·74	52·7	6	54	64·6	5+1	64·8	2·033	2·037

Before leaving this section we would sum up some of the principal facts observed. In the first place, it is of much importance to know that these salts dissolve in water without increasing its bulk more than is due to the water attached to them as crystallized water. The acid and bases entirely disappear in the water which is attached to them; and so closely does this rule prevail, that the atom of basic water in the tribasic arseniates and phosphates has ceased to play the part of water, either in solution or in the solid state. In the condition of solid salts, we find four classes to which we have drawn attention. The first of these is represented by salts having their water firmly attached, and possess as a divisor for their atomic volume a number equal or approaching to 11; and we have concluded, as the quotient of this divisor is always the same as the number of atoms of water attached to the salt, that 11 is the volume of an atom of water in combination; and hence that the salts have disappeared in this attached water, adding to its weight, but not to its observed bulk.

The second class of salts in this section is represented by potash alum, in which the astonishing result is obtained, that the 23 anhydrous atoms of this salt have combined in some way with the 24 atoms of water, so as to cease to occupy bulk in solution. The peculiarity of this group is, that an additional 11 becomes attached to the solid salt, so that the quotient of the divisor is 25 instead of 24. This fact, and that connected with the ammoniacal alums in the same group, cannot be discussed with propriety in the present place.

The third group of salts in this section is one of high interest, and is represented by salts having their hydrate water attached by a feeble affinity. In them the volume of the

water is exactly the same as that of ice itself. Sugar belongs to this category, not because the H_{11} O_{11} are feebly attached, for it has yet to be shown that they are present *quasi* water. The fact however that these 11 atoms of hydrogen and oxygen take up the same space as liquid water in solution, and as ice in the solid state of sugar, and that the 12 atoms of carbon have ceased to occupy space, is a matter of supreme interest, and cannot fail to lead to important results when we come to the consideration of organic compounds.

The fourth class in this section finds its representatives in the sulphates of the magnesian class of metals, and perhaps ought to include the magnesian chlorides also. They possess their constitutional water with the usual volume of 11, while the water feebly attached is present with the volume of ice.

Although, then, we have four distinct groups in the section of salts possessing a large amount of hydrate water, we have only two modifications of volume, the one represented by a number equal or approximating to 11, the other by the volume of ice itself, viz. 9·8.

We now proceed to the consideration of salts which either are destitute of water, or contain it in small proportion only. The volumes affected by them must be volumes peculiar to themselves, and not, as in the present section, to the water with which they are combined.

Section II.

Sulphates with a small proportion of Water of Hydration, Anhydrous and Double Sulphates.

Sulphate of Potash, KO, SO_3 = 87·25.—Half an equivalent of this salt, dissolved in 3140 grains of water of 37°, increased 7·2, and at 80°, 9·0; the same quantity dissolved in 1000 grains of water at 66°, increased 9·0.

I. II. KO, SO_3, vol. in solution 18·0

A whole equivalent of the salt being placed in its saturated solution effected a rise in the stem of 33·0 at a temperature of 55°; and a repetition of the experiment gave the increase 33·1.

			Sp. gr.
I.	KO, SO_3, vol. of salt	33·0 ...	2·644
II.	... ...	33·1 ...	2·636
	Mean . .	33·05	2·640

Sulphate of Potash and Sulphate of Water, KO, SO_3 + HO, SO_3 = 136·35.—The fourth of an equivalent (34·08 grains), being dissolved in 1000 grains of water, caused an increase of

9·0 at a temperature of 59°, and 33 grains dissolved in the same quantity of water occasioned a rise of 8·75 at 44°.

I.	$KO, SO_3 + HO, SO_3$, vol. in solution	36·0
II.	... ...	36·1
	Mean . .	36·05

Half an equivalent (68·2 grains) of the salt, previously fused, immersed in a saturated solution, produced a rise in the stem of 27·5; and a second experiment with the same quantity, but with salt which had not been fused, of 27·6, the temperature on both occasions being 55°.

			Sp. gr.
I.	$KO, SO_3 + HO, SO_3$, vol. of salt	55·0 ...	2·479
II.	... ...	55·2 ...	2·470
	Mean . .	55·1 ...	2·475

Sulphate of Ammonia, $NH_4O, SO_3 + HO = 75·25$.—In three separate experiments, in which 75·25 grains of this salt were dissolved in 1000 grains of water, the increase was exactly 36·0 at 60°.

I. II. III. NH_4O, SO_3HO, vol. in solution 36·0

Half an equivalent (37·6 grains) being immersed in a saturated solution at 49°, caused, in two experiments, an increase of 21·5.

			Sp. gr.
I. II.	$NH_4O, SO_3 + HO$, vol. of salt	43·0 ...	1·750

Sulphate of Ammonia and Sulphate of Water, $NH_4O, SO_3 + HO, SO_3 = 115.35$.—Half an equivalent (57·7 grains) of this salt, dissolved in 1000 grains of water, gave a rise in the stem of 23·0 at 56°, in two separate experiments.

I. II. $NH_4O, SO_3 + HO, SO_3$, vol. in solution 46·0

The same quantity of salt being placed in its saturated solution, caused an increase of 32·5 in one experiment and of 33 0 in a second, the temperature in both cases being 58°.

			Sp. gr.
I.	$NH_4O, HO, 2SO_3$, vol. of salt	65·0 ...	1·775
II.	... ...	66·0 ...	1·747
	Mean . .	65·5 ...	1·761

Sulphate of Soda and Sulphate of Water, $NaO, SO_3 + HO, SO_3 = 120·64$.—The fourth of an equivalent (30·16 grains) dissolved in 1000 grains of water, in the first experiment with an increase of 4·6, in the second of 4·7, both at a temperature of 56°.

I.	$NaO, SO_3 + HO, SO_3$, vol. in solution	18·4
II.	... ...	18·8
	Mean . .	18·6

The same quantity of salt thrown into a saturated solution caused, in two experiments, an increase of 11·0 at a temperature of 54°.

			Sp. gr.
I. II.	Bisulphate of soda, vol. of salt	44·0 ...	2·742

Ammoniacal Sulphate of Copper, $CuO, SO_3, HO + 2NH_3 = 123{\cdot}0$.—The fourth of an equivalent (30·8 grains) of this substance in beautiful large indigo-blue crystals, dissolved in 1000 grains of water, with an increase of 13·3 in one experiment and 13·0 in another, the temperature being 54 and 50°.

I.	$CuO, SO_3, HO + 2NH_3$, vol. in solution	53·2
II.	... ...	52·0
	Mean . .	52·6

61·5 grains of this salt placed in the solution from which it had crystallized, caused an increase of 34·3, and on a repetition of the experiment of 34·4, at a temperature of 60°.

				Sp. gr.
I.	$CuO, SO_3, HO + 2NH_3$, vol. of salt	68·6	...	1·793
II.	... ...	68·8	...	1·788
	Mean . .	68·7	...	1·790

Sulphate of Copper and Sulphate of Potash, $CuO, SO_3 + KO, SO_3 + 6HO = 221{\cdot}31$.—The fourth of an equivalent (55·32 grains) dissolved in 3140 grains of water at 32°, increased to 16·3, and at 72° to 18·0.

	$CuO, SO_3 + KO, SO_3 + 6HO$, vol. in solution 72·0

The same quantity of the salt placed in its saturated solution, caused an increase of 24·7 in one experiment and of 24·6 in a second, the temperature on both occasions being 55°.

				Sp. gr.
I.	$CuO, SO_3 + KO, SO_3 + 6HO$, vol. of salt	98·8	.	2·239
II.	... ...	98·4	.	2·249
	Mean . .	98·6	.	2·244

Sulphate of Copper and Sulphate of Ammonia, $CuO, SO_3 + NH_4O, SO_3 + 6HO = 199{\cdot}88$.—On dissolving 50 grains of this salt in 1000 grains of water, an increase was occasioned in the first experiment of 20·2, in the second of 20·3, both at a temperature of 59°.

I.	Sulphate of copper and ammonia, vol. in solution	80·8
II.	... ...	81·2
	Mean . .	81·0

On immersing the same quantity in a saturated solution, an

increase of 26·4 was obtained in the first experiment, and of 26·45 in the second, both at a temperature of 59°.

			Sp. gr.
I.	$CuO, SO_3 + NH_4O, SO_3 + 6HO$, vol. of salt	105·6 ..	1·892
II.	... ...	105·8 .	1·889
	Mean . .	105·7 ..	1·891

Sulphate of Zinc and Sulphate of Potash, $ZnO, SO_3 + KO, SO_3 + 6HO = 221·86$.—The fourth of an equivalent of this salt (55·46 grains), on being dissolved in 1000 grains of water, increased to 18 at a temperature of 60° in two experiments.

I. II. $ZnO, SO_3 + KO, SO_3 + 6HO$, vol. in solution 72.

The same quantity immersed in a saturated solution, caused an increase also in two experiments of 24·7, the temperature being 56°.

			Sp. gr.
I. II.	$ZnO, SO_3 + KO, SO_3 + 6HO$, vol. of salt	98·8 ...	2·245

Sulphate of Zinc and Sulphate of Ammonia, $ZnO, SO_3 + NH_4O, SO_3 + 6HO = 200$.—On dissolving 45 grains of this salt in 1000 of water, an increase of 18·0 was occasioned in three separate experiments at a temperature of 58°.

I. II. III. $ZnO, SO_3 + NH_4O, SO_3 + 6HO$, vol. in solution 80

On adding the fourth of an equivalent (50 grains) to a saturated solution, an increase of 26·4 was occasioned in the first experiment, and of 26·3 in the second, both at a temperature of 55°.

			Sp. gr.
I.	Sulph. zinc and ammonia, vol. of salt	105·6 ...	1·894
II.	... ...	105·2 ...	1·901
	Mean . .	105·4 ...	1·897

Sulphate of Magnesia and Sulphate of Potash, $MgO, SO_3 + KO, SO_3 + 6HO = 202·29$.—When a quarter of an equivalent of this salt (50·57 grains) is dissolved in as many as 3140 grains of water, the volume at 32° is only 15·45, but is 18 at 80°. This gives for the salt in very dilute solution—

$MgO, SO_3 + KO, SO_3 + 6HO$, vol. in solution	63 at 40°
... ...	72 at 80°

The same quantity of salt after immersion in a saturated solution gave in the first experiment an increase of 24·3, and in the second of 24·4, both at a temperature of 57°.

			Sp. gr.
I.	Sulph. magnesia and potash, vol. of salt	97·2 .	2·081
II.	... ...	97·6 .	2·071
	Mean . .	97·4 .	2·076

Sulphate of Magnesia and Ammonia, $MgO, SO_3 + NH_4O, SO_3 + 6HO = 181·12$.—The fourth of an equivalent (45·28

grains) being dissolved in 1000 grains of water, caused an increase of 20·0 at 60°; and a repetition of the experiment at the same temperature gave the increase 20·1.

I.	Sulph. magnesia and ammonia, vol. in solution	80·0
II.	... ...	80·4
	Mean . .	80·2

The same quantity of salt placed in a saturated solution, gave on two occasions a rise in the stem of 26·3 at a temperature of 60°.

		Sp. gr.
I. II.	Sulph. magnesia and ammonia, vol. of salt 105·2 .	1·721

Sulphate of Iron and Potash, $FeO, SO_3 + KO, SO_3 + 6HO = 216{\cdot}73$.—The eighth of an equivalent (27·09 grains), when dissolved in 1000 of water, caused an increase of 9 at a temperature of 65°.

Sulph. iron and potash, vol. in solution 72.

The same quantity immersed in a saturated solution occasioned a rise in the stem in two experiments 12·3 at a temperature of 61°.

		Sp. gr.
I. II.	Sulph. iron and potash, vol. of salt 98·4 ...	2·202

Sulphate of Iron and Ammonia, $FeO, SO_3 + NH_4O\,SO_3 + 6HO = 195{\cdot}55$.—On dissolving 33·45 grains of this salt in 1000 of water, the increase in the first experiment was 13·4, in the second 14, both at a temperature of 59°; a third experiment with 66·9 grains, gave the increase 28 at the same temperature.

I.	Sulph. iron and ammonia, vol. in solution	78·3
II.	... ...	81·8
III.	... ...	81·8
	Mean . .	80·7

48·89 grains of the salt being projected into a saturated solution, caused in the first experiment an increase of 26·4, in the second of 26·5.

			Sp. gr.
I.	Sulph. iron and ammonia, vol. of salt	105·6 ...	1·851
II.	... ...	106·0 ...	1·845
	Mean . .	105·8 ...	1·848

In the last section we gave the volumes occupied by those salts which did not occupy any space of themselves, but merely that due to their combined water. The divisor for the volumes observed in solution was therefore necessarily 9, or the atomic volume of water itself. But in this section we have experimented upon salts which take up space quite inde-

pendent of their water of crystallization, even when they contain water, and yet the most interesting result follows, that the same divisor, 9, continues for the volumes ascertained by experiment. The volumes in solution of the salts examined, allowing for errors of observation, are therefore always multiples of 9,—the atomic volume of water. The volumes of the solids are, like those of the previous section, multiples of one and the same number, that number being also, as in the former case, 11; but the ammonia salts do not arrange themselves under this divisor for reasons which will be explained presently. The averages of the experiments on all the salts are thrown into the following table, into which is also introduced the exact numbers which would have resulted had there been a strict accordance with the law obviously indicated by experiment.

TABLE VI.—Showing the volumes of certain Sulphates with a small proportion of Water of Hydration, Anhydrous and Double Sulphates.

Designation.			Volume in solution.			Volume in state of salt.				
Name.	Formula.	Atomic weight.	Volume in solution by experiment.	9, or volume of water as unity.	Volume by theory.	Volume of salt by experiment.	11, or supposed vol. of combined water as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Sulphate of potash..	KO, SO_3	87·25	18·0	2	18	33·05	3	33	2·644	2·640
Bisulphate of potash.	$KO, SO_3 + HO, SO_3$	136·35	36·05	4	36	55·1	5	55	2·479	2·475
Sulphate of ammonia	$NH_4O, SO_3 + HO$	75·25	36·0	4	36	43·0	4	44	1·710	1·750
Bisulphate of ammonia.....	$NH_4O, SO_3 + HO, SO_3$	115·35	46·0	5	45	65·5	6	66	1·747	1·761
Bisulphate of soda...	$NaO, SO_3 + HO, SO_3$	120·64	18·6	2	18	44·0	4	44	2·742	2·742
Ammoniacal sulphate of copper	$CuO, SO_3HO + 2NH_3$	123·00	52·6	6	54	68·7	...	...	.....	1·790
Sulphate of copper and potash.....	$CuO, SO_3 + KOSO_3 + 6HO$	221·31	72·0	8	72	98·6	9	99	2·235	2·244
Sulphate of copper and ammonia...	$CuO, SO_3 + NH_4O, SO_3 + 6HO$	199·88	81·0	9	81	105·7	9	99	2·019	1·891
Sulphate of zinc and potash.....	$ZnO, SO_3 + KO, SO_3 + 6HO$	221·86	72·0	8	72	98·8	9	99	2·241	2·245
Sulphate of zinc and ammonia...	$ZnO, SO_3 + NH_4O, SO_3 + 6HO$	200·00	80·0	9	81	105·4	9	99	2·020	1·897
Sulphate of magnesia and potash	$MgO, SO_3 + KO, SO_3 + 6HO$	202·29	72·0	8	72	97·4	9	99	2·043	2·076
Sulphate of magnesia & ammonia	$MgO, SO_3 + NH_4O, SO_3 + 6HO$	181·12	80·2	9	81	105·2	9	99	1·829	1·721
Sulphate of iron and potash	$FeO, SO_3 + KO, SO_3 + 6HO$	216·73	72·0	8	72	98·4	9	99	2·190	2·202
Sulphate of iron and ammonia...	$FeO, SO_3 + NH_4O\ SO_3 + 6HO$	195·55	80·7	9	81	105·8	9	99	1·975	1·848
Sulphate of nickel and potash.....	$NiO, SO_3 + KO, SO_3 + 6HO$	218·99	71·5	8	72	100·0	9	99	2·212	2·190

The correspondence between the observed and calculated results in the preceding table, as far as regards the potash salts, is so striking as to remove any doubt of the basis upon which the calculations are made. It is therefore of interest to consider the results indicated by the table a little more in detail. The first point of remark is, that in every case the ammoniacal salt has one volume greater in solution than the corresponding potash salt. Sulphate of potash possesses two volumes in solution; sulphate of ammonia divested of one volume for its atom of water possesses three. These volumes are respectively carried through the whole class of double sulphates. The volumes of these double sulphates are made up of the sum of the volumes of their constituent salts, which appear, therefore, to be united unchanged. We saw in the previous section that the magnesian sulphates dissolve in water without increasing its bulk more than is due to their water of combination. The same takes place in their double sulphates, for subtracting the volumes of the atoms of water which have been carried by the sulphates into their union with sulphate of potash, the remainder shows the volumes belonging to the latter salts, as indicated by direct experiment. This is strikingly exemplified also by bisulphate of soda. Sulphate of soda was shown in the last section to possess no volume in solution, and in this acid salt we find that the sulphate of soda has in solution ceased to occupy space, for the resulting volume of the acid salt is only 18 or 9×2, which is the atomic volume of sulphate of water, as ascertained by the volume occupied by it in bisulphate of potash and bisulphate of ammonia, and as determined also by a calculation, which we have made, of the volume occupied by hydrated sulphuric acid in a *dilute* solution, founded upon recorded specific gravities.

Although the ammoniacal sulphates, on account of their analogy to the potash salts, have been introduced into the above table, it is obvious that the numbers representing their volumes are too wide from the theoretical numbers to be considered multiples of 11. Hydrated sulphate of ammonia affects four volumes, 11×4, but the anhydrous salt obeys a different law. On immersing in turpentine 33·15 grains of anhydrous NH_4O, SO_3, the increase was 19·6 and 19·5, the mean being 19·55 water-grain measures. This gives 39·1 as the vol. of the equivalent, and $9{\cdot}8 \times 4 = 39{\cdot}2$. Anhydrous sulphate of ammonia affects, therefore, 4 vol. of ice; and the double salts consist of the magnesian sulphates with 6 equivalents of water attached to an equivalent of anhydrous sulphate of ammonia, as will be seen from the following table of their solid volumes and specific gravities.

Name.	Solid volume by experiment.	Solid volume by theory.	Specific gravity by experiment.	Specific gravity by theory.
Sulphate of ammonia.....	39·1	39·2	1·695	1·691
Sulphate of copper and ammonia.....	105·7	105·2	1·891	1·900
Sulphate of zinc and ammonia.....	105·4	105·2	1·887	1·901
Sulphate of magnesia and ammonia...	105·2	105·2	1·721	1·721
Sulphate of iron and ammonia.....	105·8	105·2	1·848	1·858

As one of the members of the group of double salts here described takes up no space of itself, it became of importance to ascertain the volume of the salt when deprived of water, and also the space occupied by the double salt reduced to the same state. In this examination it was quite unnecessary to obtain the volumes in solution, because it was obvious that salts not occupying in solution a greater volume than that due to their water of hydration, would, in their anhydrous condition, take up no space at all. In fact, we had ascertained that not only was there no increase in dissolving such salts in water, but that actually there was a contraction if the water were in large proportion to the salt; when this is not the case, the increased expansibility of the solution prevents the contraction being observed.

In the following examination will be found almost all the salts previously described in their hydrated condition, with the exception of the phosphates and arseniates, which we reserve for another paper.

Sulphate of Magnesia, $MgO, SO_3 = 60{\cdot}86$.—Half an equivalent of this salt, 30·43 grains, thrown into turpentine, caused an increase of 11·0; but in a second experiment the increase was 11·5, the temperature in both cases being 65°.

			Sp. gr.
MgO, SO_3, vol. of salt	22·0	...	2·766
... ...	23·0	...	2·646
Mean . .	22·5	...	2·706

Sulphate of Zinc, $ZnO, SO_3 = 80{\cdot}43$.—Half an equivalent of this salt, 40·22 grains, projected into turpentine, caused an increase of 11·05 and, in another experiment, of 10·8.

			Sp. gr.
ZnO, SO_3, vol. of salt	22·1	...	3·639
... ...	21·6	...	3·723
Mean . .	21·85	...	3·681

Sulphate of Copper, $CuO, SO_3 = 79{\cdot}88$.—Half an equivalent, 39·94 grains, of the salt placed in turpentine, caused in several successive experiments an increase of exactly 11·0.

		Sp. gr.
CuO, SO_3, vol. of salt 22·0	...	3·631

Sulphate of Iron, $FeO, SO_3 = 75·3$.—Half an equivalent of this salt, 37·65 grains, caused, in two experiments with the same salt, a rise of 12·0, which gives for the equivalent 24·0 and a specific gravity of 3·138.

Sulphate of Cobalt, $CoO, SO_3 = 77·69$.—On immersing 19·42 grains of this salt in turpentine, an increase of 5·5 was obtained in two experiments; this gives for the equivalent 22·0, and for the specific gravity 3·531.

Sulphate of Soda, $NaO, SO_3 = 71·43$.—On throwing a whole equivalent of this salt into turpentine, the increase was only 27·5 in several successive experiments, which gives for the specific gravity 2·597. Karsten found its specific gravity to be 2·631, a result approximating to our own; attention is drawn to this circumstance because both results are anomalous.

Sulphate of Silver, $AgO, SO_3 = 156·48$.—On immersing in turpentine 78·24 grains of this salt, the increase was 14·7, which gives as the volume of the equivalent 29·4, and a specific gravity of 5·322.

Chromate of Silver, $AgO, CrO_3 = 168·49$.—The fourth of an equivalent of this salt, 42·12 grains, gave an increase, when thrown into turpentine, of 7·3 in two successive experiments. This gives 29·2 for the volume of the equivalent, and 5·770 for the specific gravity of the salt.

Sulphate of Copper and Potash, $CuO, SO_3 + KO, SO_3 = 167·31$.—41·82 grains, the fourth of an equivalent, thrown into turpentine, caused an increase of 14·9 in one experiment and of 15·0 in another, the temperature in both cases being 54°.

		Sp. gr.
$CuO, SO_3 + KO, SO_3$, vol. of salt 59·6	...	2·807
... ... 60·0	...	2·788
Mean . . 59·8	...	2·797

Sulphate of Nickel and Potash, $NiO, SO_3 + KO, SO_3 = 164·99$.—41·54 grains caused an increase of 14·2 in one experiment and 14·5 in a second, the temperature in both cases being 54°.

		Sp. gr.
$NiO, SO_3 + KO, SO_3$, vol. of salt 56·4	...	2·925
... ... 57·5	...	28·69
Mean . . 56·95	...	2·897

Sulphate of Zinc and Potash, $ZnO, SO_3 + KO, SO_3 = 167·86$.—41·96 grains, the fourth of an equivalent, placed in turpentine, caused an increase of 14·9 in two experiments.

		Sp. gr.
$ZnO, SO_3 + KO, SO_3$, vol. of salt	59·6 ...	2·816

Sulphate of Magnesia and Potash, $MgO, SO_3 + KO, SO_3 = 148·29$.—37·07 grains, or the fourth of an equivalent, caused in one experiment an increase of 13·9, and in a second of 13·8, the temperature being 55°.

		Sp. gr.
$MgO, SO_3 + KO, SO_3$, vol. of salt	55·6 ...	2·667
... ...	55·2 ...	2·686
Mean . .	55·4 ...	2·676

Sulphate of Manganese and Potash, $MnO, SO_3 + KO, SO_3 = 163·07$.—40·8 grains of this salt, one-fourth of an equivalent, placed in turpentine, caused an increase of 13·5 in one experiment and 13·6 in another, at a temperature of 55°.

		Sp. gr.
$MnO, SO_3 + KO, SO_3$, vol. of salt	54·0 ...	3·020
... ...	54·4 ...	2·996
Mean . .	54·2 ...	3·008

Sulphate of Copper and Ammonia, $CuO, SO_3 + NH_4O, SO_3 = 145·88$.—36·53 grains of this salt thrown into turpentine, caused an increase of 16·7 in one experiment and 16·6 in another, at a temperature of 60°.

		Sp. gr.
I. Sulphate of copper and ammonia	66·6 ...	2·190
II.	66·2 ...	2·204
Mean . .	66·4 ...	2·197

Sulphate of Zinc and Ammonia, $ZnO, SO_3 + NH_4O, SO_3 = 146·0$.—30 grains of this salt thrown into turpentine, caused an increase of 13·5 at 60°.

		Sp. gr.
Sulphate of zinc and ammonia, vol. of salt	65·7 ...	2·222

Sulphate of Magnesia and Ammonia, $MgO, SO_3 + NH_4O, SO_3 = 127·12$.—The fourth of an equivalent (31·78 grains) placed in turpentine, caused an increase of 16·5 in the first experiment, and of 16·4 in the second.

		Sp. gr.
I. Sulphate of magnesia and ammonia	66·0 ...	1·926
II.	65·6 ...	1·938
Mean . .	65·8 ...	1·932

Sulphate of Alumina, $Al_2O_3 3SO_3 = 171·95$.—This salt, and the anhydrous alums, offer difficulties to the correct estimation of their specific gravity on account of their great porosity and liability to carry down air. The best mode of obviating this source of error is to introduce a metallic wire previously

moistened with turpentine into the volumenometer, and employ this to break the numerous air bubbles which arise on immersing the salts. The following estimations were taken with great care, but from this source of error may possibly be inaccurate.

The eighth part of an equivalent (21·49 grains), immersed in turpentine and treated as described above, gave results varying from 9·8 to 10·0, the mean result being 9·9.

			Sp. gr.
$Al_2O_3 3SO_3$, vol. of salt	79·2	...	2·171

Sulphate of Alumina and Potash, $Al_2O_3 3SO_3 + KO, SO_3 = 259{\cdot}36$.—The eighth part of an equivalent (32·42 grains) of anhydrous alum, immersed in turpentine and treated as described in the case of sulphate of alumina, gave an increase of 14·5 and 14·6 in two experiments.

			Sp. gr.
I. Alum, vol. of salt	116·0	...	2·236
II.	116·8	...	2·220
Mean . .	116·4	...	2·228

Ammonia Alum, $Al_2O_3 3SO_3 + NH_4O, SO_3 = 238{\cdot}2$.—The eighth part of an equivalent of this salt (29·77 grains), treated as in the previous cases, gave an increase of 14·6 in two experiments.

			Sp. gr.
Ammonia alum, vol. of salt	116·8	...	2·039

Carbonate of Soda, $NaO, CO_2 = 53{\cdot}47$.—The equivalent of this salt, thrown into turpentine, gave an increase of exactly 22·0, which makes its specific gravity 2·430.

Chloride of Magnesium, $MgCl = 48{\cdot}12$.—The anhydrous chloride of magnesium used in the experiment was made by saturating equal portions of muriatic acid with magnesia and ammonia, mixing together, evaporating to dryness, and heating to redness.

Half an equivalent (24·06 grains), thrown into turpentine, caused an increase of 11·0 in one experiment and of 11·1 in a second.

			Sp. gr.
I. MgCl, vol. of salt	22·0	...	2·187
II.	22·2	...	2·167
Mean . .	22·1	...	2·177

Chloride of Calcium, $CaCl = 55{\cdot}92$.—This salt was rendered anhydrous by fusing it in a platinum crucible for some time. 28 grains of the fused salt, thrown into turpentine, caused an increase of 11·3 at a temperature of 63°.

			Sp. gr.
CaCl, vol. of salt	22·5	...	2·480

Chloride of Cobalt, CoCl = 65·0.—On throwing the fourth of an equivalent (16·25 grains) of anhydrous chloride of cobalt into turpentine, an increase of 5·5 was obtained in two experiments, and of 5·6 in a third trial.

				Sp. gr.
I.	CoCl, vol. of salt	22·0	...	2·954
II.	... ...	22·0	...	2·954
III.	... ...	22·4	...	2·902
	Mean . .	22·13	...	2·937

TABLE VII.—Showing the volume occupied by certain Hydrated Salts rendered Anhydrous.

Designation.			Volumes of anhydrous salts.				
Name.	Formulæ.	Atomic weight.	Volume of salt by experiment.	11, taken as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Sulphate of magnesia	MgO, SO_3	60·86	22·5	2	22	2·766	2·706
Sulphate of zinc	ZnO, SO_3	80·43	21·85	2	22	3·656	3·681
Sulphate of copper...	CuO, SO_3	79·88	22·0	2	22	3·631	3·631
Sulphate of iron.....	FeO, SO_3	75·3	24·0	2	22	3·423	3·138
Sulphate of cobalt ...	CoO, SO_3	77·69	22·0	2	22	3·531	3·531
Sulphate of soda.....	NaO, SO_3	71·43	27·5	...	...	...	2·597
Sulphate of silver ...	AgO, SO_3	156·48	29·4	...	...	...	5·322
Chromate of silver...	AgO, CrO_3	168·49	29·2	...	...	...	5·770
Sulphate of alumina .	$Al_2O_3 3SO_3$	171·95	79·2	...	...	...	2·171
Sulphate of copper and potash	CuO, SO_3+KO, SO_3	167·31	59·8	5	55	3·042	2·797
Sulphate of nickel and potash	NiO, SO_3+KO, SO_3	164·99	56·95	5	55	2·998	2·897
Sulphate of zinc and potash	ZnO, SO_3+KO, SO_3	167·86	59·6	5	55	3·034	2·816
Sulphate of magnesia and potash	MgO, SO_3+KO, SO_3	148·29	55·4	5	55	2·694	2·676
Sulphate of manganese and potash.	MnO, SO_3+KO, SO_3	163·07	54·2	5	55	2·964	3·008
Sulphate of copper and ammonia ...	CuO, SO_3+NH_4O, SO_3	145·88	66·4	6	66	2·192	2·197
Sulphate of zinc and ammonia ...	ZnO, SO_3+NH_4O, SO_3	146·0	65·7	6	66	2·212	2·222
Sulphate of magnesia and ammonia	MgO, SO_3+NH_4O, SO_3	127·0	65·8	6	66	1·924	1·932
Potash alum	$Al_2O_3 3SO_3+KO, SO_3$	259·36	116·4	...	...	...	2·228
Ammonia alum	$Al_2O_3, 3SO_3+NH_4O\ SO_3$	238·2	116·8	...	...	...	2·039
Carbonate of soda ...	NaO, CO_2	53·47	22·0	2	22	2·427	2·427
Chloride of cobalt ...	Co, Cl	65·0	22·1	2	22	2·955	2·937
Chloride of magnesium.....	Mg, Cl	48·12	22·1	2	22	2·187	2·177
Chloride of calcium .	Cu, Cl	55·92	22·5	2	22	2·542	2·485

The preceding table exhibits various points of great interest as regards isomorphism. Hydrogen has for a long time been recognised by chemists as equivalent to a magnesian metal; and hence the sulphate of a metal of this class should possess the volume of sulphate of water. The volume of bisulphate of potash is 55·0 by experiment, which leaves 22·0 for that of sulphate of water, on deducting the volume of sulphate of potash, which is 33·0; and the same result follows when the volume of sulphuric acid is deduced from bisulphate of soda, if we suppose the sulphate of soda to enter that salt with two volumes. Thus we have —

Sulphate of water . . . . = 22 ÷ 11 = 2
Sulphate of a magnesian oxide = 22 ÷ 11 = 2

We now see that bisulphate of potash (sulphate of water and sulphate of potash) is exactly equivalent to the double sulphates of the magnesian class. (*Vide* Section V.)

Bisulphate of potash ($HO, SO_3 + KO, SO_3$) = 55
Sulphate of magnesia and potash ($MgO, SO_3 + KO, SO_3$) = 55.

It is now comprehensible why bisulphate of soda should have a volume of 44·0 in the solid state and only of 18·0 in a state of solution; because sulphate of soda which assumes a volume in the solid state becomes added to the same volume possessed by sulphate of water, while in the state of solution the proper volume of sulphate of soda disappears altogether.

Bisulphate of ammonia possesses a volume due to a combination of sulphate of water and sulphate of ammonia, with a volume of 11 × 4, and it will be observed that the same result attends the double sulphates of the magnesian metals with sulphate of ammonia.

Bisulphate of ammonia ($NH_4O, SO_3 + HO\ SO_3$) = 66
Sulphate of ammonia and copper ($NH_4O, SO_3 + CuO, SO_3$) = 66.

The cause of this singular result is in the mutual convertibility of the primitive volumes 9·8 and 11.

It is very curious to observe the large number of volumes which have disappeared when the salt combines with water. Thus sulphate of alumina in its anhydrous state possesses a bulk equal to 79·2, which has ceased to occupy space in the hydrated salt; and still more remarkable instances of this are seen in the alums, which add to this the volumes of their alkaline sulphates. A curious result obtained in the examination of the hydrated alums is now explicable. We found that the potash alums took up in solution only the space due to their water; but that the space occupied by them in the state of salts was one volume in addition to this quantity. In the pre-

ceding section we observed that sulphate of potash possessed the singular property of expanding one volume in becoming solid; 9×2 in a state of solution becoming 11×3 in the state of a salt. It is impossible to refrain from accepting this as an explanation of the increase of one in the quotient obtained by dividing the volumes by their proper numbers 9 and 11—24×9 becoming 25×11.

The difficulties, to which we have already alluded, prevent us placing much confidence in our results for the anhydrous alums. Sulphate of alumina seems to affect eight volumes of ice, $9{\cdot}8 \times 8 = 78{\cdot}4$; in ammonia alum the latter becomes united to the volume of anhydrous sulphate of ammonia, $9{\cdot}8 \times 8 + 9{\cdot}8 \times 4 = 117{\cdot}6$; while potash alum should consist of $9{\cdot}8 \times 8 + 11 \times 3 = 111{\cdot}4$. It is unnecessary to remark that these theoretical numbers possess only an approximation to our experimental results. (*Vide* remarks on Section V.)

The sulphates of soda and silver and the corresponding chromate are also obviously exceptions to the general rule of the solid volume being multiples of 11. But in the last section we had similar exceptions in salts which ranged themselves under 9·8 or the volume of ice. The sulphates now under consideration have the same divisor, if sulphate of soda be not considered an exception, as the variation is decidedly too great to be attributed to a mere error of experiment; it ought however to be observed that Mohs gives for the specific gravity of this salt 2·462, a number much more in accordance with theory than our own result; but as our experiments have been often repeated, they may perhaps be viewed as an argument in favour of an opinion, deduced from other considerations, that sulphate of soda has a double atom $27{\cdot}5 \times 2 = 55$, which is 11×5.

Name.	Volume by experiment.	9·8, or volume of ice as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Sulphate of soda	27·5	3	29·4	2·430	2·597
Sulphate of silver	29·4	3	29·4	5·322	5·322
Chromate of silver.....	29·2	3	29·4	5·711	5·770

Section III.

Nitrates, &c.

The nitrates do not in general affect a large proportion of water of hydration, and are therefore well-calculated to show

the volume occupied by anhydrous salts. It will be observed that they present some peculiarities.

Nitrate of Potash, KO, NO_5=101·3.—The half of an equivalent of this salt, 50·65 grains, being dissolved in 1000 grs. of water, gave an increase of 18·05 at 45°.

KO, NO_5, vol. in solution 36·1

The same quantity of salt, 50·65 grains, thrown into turpentine, caused a rise in the stem of 24·5, 24·4, 24·5 in three successive experiments.

				Sp. gr.
I.	KO, NO_5, vol. of salt	49·0	...	2·067
II.	... ...	48·8	...	2·075
III.	... ...	49·0	...	2·067
	Mean . .	48·9	...	2·070

Nitrate of Ammonia, NH_4O, NO_5=80·3.—The volume of nitrate of ammonia in solution was determined by dissolving 40·15 grains of this salt in 1000 grains of water. In one experiment the increase in the stem was 22·5, the temperature being 57°; in a second the rise was 23·0 at 63°.

I.	NH_4O, NO_5, vol. in solution	45·0
II.	... ...	46·0
	Mean . .	45·5

Half an equivalent of this salt, well-dried (40.15 grains), on being immersed in turpentine produced an increase in three experiments of 24·7, 24·5, 24·5.

				Sp. gr.
I.	NH_4O, NO_5, vol. of salt	49·4	...	1·625
II.	... ...	49·0	...	1·639
III.	... ...	49·0	...	1·639
	Mean . .	49·1	...	1·635

Nitrate of Soda, NaO, NO_5=85·45.—On dissolving 85·45 grains, or one equivalent, of this salt in 1000 grains of water, an increase of 27·1 was obtained, the temperature being 59°; but on repetition of the experiment at the same temperature the increase was only 26·0.

I.	NaO, NO_5, vol. in solution	27·1
II.	... ...	26·0
	Mean . .	26·5

The half of an equivalent of this salt, 42·72 grains, well-dried, produced an increase on being thrown into turpentine of 19·6 in three experiments and 19·5 in a fourth trial.

				Sp. gr.
I.	NaO, NO_5	vol. of salt	39·2 ...	2·180
II.	...	...	39·2 ...	2·180
III.	...	...	39·2 ...	2·180
IV.	...	...	39·0 ...	2·190
		Mean . .	39·1	2·182

Nitrate of Silver, $AgO, NO_5 = 170·0$.—On dissolving 42·5 grains of this salt in 1000 grains of water, an increase of 6·8 was effected at a temperature of 59°.

AgO, NO_5, vol. in solution 27·2.

The same quantity of salt, 4·25 grains, thrown into turpentine, produced an increase of 9·8.

			Sp. gr.
AgO, No_5	vol. of salt	39·2 ...	4·336

Nitrate of Lead, $PbO, NO_5 = 165·75$.—This salt gives very unsatisfactory results on being dissolved in water; at low temperatures the volume for the atom is equal to nearly 18·0, or 9×2. But at higher temperatures the volume in solution approaches nearly to 27·0, or 9×3; and, although the results do not come out exact, unless corrected for expansion, we are inclined to view the latter as the true result. 83 grs. dissolved in water gave an increase of 12·5; in a second experiment of 12·7, both at a temperature of 65°.

PbO, NO_5, vol. in solution		25·0
...	...	25·4
	Mean . .	25·2

The fourth part of an equivalent, 41·43 grains, immersed in turpentine, gave an increase of 9·7; 82·87 grains gave the increase 19·2; and in a third experiment 19·0.

				Sp. gr.
I.	PbO, NO_5,	vol. of salt	38·8 ...	4·272
II.	...	...	38·4 ...	4·316
III.	...	...	38·0 ...	4·362
		Mean . .	38·4 ...	4·316

Nitrate of Barytes, $BaO, NO_5 = 130·85$.—Half an equivalent of this salt, 65·42 grains, dissolved in 1000 grains of water with an increase of 13·5 at a temperature of 60°; and a repetition of the experiment was attended with the same result.

BaO, NO_5, vol. in solution 27·0.

The same quantity of salt, immersed in turpentine, caused an increase of 19·8 in three experiments, and 20·0 and 20·2 in two other experiments; the salts being all different specimens, and decrepitated previously to the experiment.

			Sp. gr.
I.	BaO, NO_5, vol. of salt	39·6 ...	3·304
II.	... ...	39·6 ...	3·304
III.	... ...	39·6 ...	3·304
IV.	... ...	40·0 ...	3·271
V.	... ...	40·4 ...	3·238
	Mean . .	39·84 ...	3·284

Nitrate of Strontia = 106·0.—Half an equivalent of this salt, 53 grains, was dissolved in 1000 grains of water, with an increase of 13·0, the temperature being 62°; 106 grains dissolved in 1000 grains of water, with an increase of 27·0 at a temperature of 63°.

I.	SrO, NO_5, vol. in solution	26·0
II.	... ...	27·0
	Mean . .	26·5

53 grains immersed in turpentine gave an increase of 19·6; and this result was confirmed by a second experiment.

		Sp. gr.
SrO, NO_5, vol. of salt	39·2 ...	2·704

Nitrate of Black Oxide of Mercury, $Hg_2O, NO_5 + 2HO$ = 282·0.—This salt, in beautiful large transparent crystals, was dissolved in water containing nitric acid, to prevent the formation of a subsalt; 70·5 grains thus treated caused an increase of 13·5.

Protonitrate of mercury, vol. in solution 54·0

On immersing the same quantity of salt in turpentine, the increase in three experiments was 14·8, 14·7, and 14·7.

			Sp. gr.
I.	Protonitrate of mercury, vol. of salt	59·2 ...	4·763
II.	... ...	58·8 ...	4·796
III.	... ...	58·8 ...	4·796
	Mean . .	58·9 ...	4·785

Nitrate of Copper, $CuO, NO_5 + 3HO = 120·8$.—Half an equivalent (60·4 grains) dissolved in 1000 grains of water with an increase of 22·4 at 60°, and in a second experiment of 22·6; in a third experiment, 30·2 grains, dissolved in the same quantity of water, gave an increase of 11·4.

I.	CuO, NO_5, vol. in solution	44·8
II.	... ...	45·2
III.	... ...	45·6
	Mean . .	45·2

In two experiments, 60·4 grains thrown into turpentine

caused an increase of 29·5, which gives for an equivalent of the salt the volume 59·0, and a specific gravity 2·047.

Nitrate of Magnesia, $MgO, NO_5 + 6HO = 128·8$.—The fourth part of an equivalent of crystallized nitrate of magnesia (32·2 grains) dissolved in 1000 grains of water at 60°, with an increase of 18·1 and 18·3 in two experiments.

I.	$MgO, NO_5 + 6HO$, vol. in solution	73·2
II.	... ...	72·4
	Mean . .	72·8

The same quantity thrown into turpentine produced an increase of 22·0, which gives for the volume of an equivalent of the salt 88·0, and for its specific gravity 1·464.

Nitrate of Bismuth, $BiO, NO_5 + 3HO = 160·33$.—This salt, being decomposed when thrown into water, is not fitted for determining volume by solution; but when 80·16 grains were thrown into turpentine, the increase was obtained in two experiments of 29·2 and of 29·4.

			Sp. gr.
I.	$BiO, NO_5 + 3HO$, vol. of salt	58·4 ...	2·745
II.	... ...	58·8 ...	2·727
	Mean . .	58·6 ...	2·736

Basic Nitrate of Mercury, $2HgO, NO_5 + 2HO = 291·0$. —This salt cannot be dissolved in water without the formation of a subsalt, unless the water is used in small proportion; it is therefore unfitted for our experiments, as far as regards the volume in solution. On immersing 68·7 grains in turpentine, an increase of 16·2 was obtained in two successive experiments. This gives 68·6 as the volume of the equivalent, and a specific gravity of 4·242.

Basic Nitrate of Lead, $2PbO, NO_5 = 277·72$.—This salt is so insoluble, that it is difficult to determine its volume in solution with any great degree of accuracy. The sixteenth part of an equivalent dissolved in 1000 grains of water gave an increase of 2·6, which seems to indicate a volume of 9×5.

69·43 grains, being immersed in turpentine, gave an increase of 12·3 in several experiments.

		Sp. gr.
Basic nitrate of lead, vol. of salt	49·2 ...	5·645

The same multiple relation of 9 is carried through all the salts of this class dissolved in water. The divisor for the solid volume is, however, different from the salts of the previous sections. Exceptional cases were pointed out in their examination, in which 9·8, or the volume of ice, became the divisor; and in the present group of salts we observe a wonderful uniformity in this respect.

TABLE VIII.—Showing the volumes occupied by certain Nitrates.

Designation.			Volume in solution.			Volume in state of salt.				
Name.	Formula.	Atomic weight.	Volume by experiment.	9 taken as unity.	Volume by theory.	Volume of salt by experiment.	9·8, or volume of ice as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Nitrate of potash ...	KO, NO_5	101·3	36·1	4	36	48·9	5	49·0	2·067	2·070
Nitrate of ammonia	NH_4O, NO_5	80·3	45·5	5	45	49·1	5	49·0	1·639	1·635
Nitrate of soda.....	NaO, NO_5	85·45	26·5	3	27	39·1	4	39·2	2·180	2·182
Nitrate of silver	AgO, NO_5	170·0	27·2	3	27	39·2	4	39·2	4·336	4·336
Nitrate of lead.....	PbO, NO_5	165·75	25·4	3	27	38·4	4	39·2	4·228	4·316
Nitrate of barytes ..	BaO, NO_5	130·85	27·0	3	27	39·8	4	39·2	3·338	3·284
Nitrate of strontia ..	SrO, NO_5	106·0	26·5	3	27	39·2	4	39·2	2·704	2·704
Nitrate of black oxide of mercury	Hg_2O, NO_5+2HO	282·0	54·0	6	54	58·9	6	58·8	4·796	4·785
Basic nitrate of mercury.....	2HgO, NO_5+2HO	291·0	...	...	...	68·6	7	68·6	4·242	4·242
Basic nitrate of lead	2PbO, NO_5	277·72	...	...	...	49·2	5	49·0	5·667	5·645
Nitrate of bismuth .	BiO, NO_5+3HO	160·33	...	...	...	58·6	6	58 8	2·727	2·736
Nitrate of copper...	CuO, NO_5+3HO	120·8	45·2	5	45	59·0	6	58·8	2·054	2·047
Nitrate of magnesia	MgO, NO_5+6HO	128·8	72·8	8	72	88·0	9	88·2	1·460	1·464

It is almost superfluous to offer any remarks upon this group of salts, especially as we shall have to consider several of them in a future section. It cannot escape attention, that the nitrates of soda, silver, lead, strontia and barytes possess the same atomic volume, as might have been expected from the isomorphism of several of them. Nitrates of soda and potash do not possess the same atomic volume, and therefore their alleged isomorphism, deduced from the observation by Frankenheim* of microscopic crystals of nitrate of potash similar to those of nitrate of soda, is highly questionable. The principal exception to the volumes of the nitrates now described being multiples of ice is that of nitrate of lead, which has a volume of 38·4, instead of 39·2; but this must be due to the nature of the salt, which comes out as unsatisfactorily in a state of solution as in the solid state.

SECTION IV.

Chlorides, Bromides and Iodides.

Chloride of Potassium, KCl = 74·7.—On dissolving 37·5 grains of this salt in 1000 grains of water, the increase was 13·3 at a temperature of 57°; a second experiment with the

* Poggendorff's *Ann.*, Band xl. S. 447.

same quantity gave the increase 13·5 at 58°; and a third experiment gave 13·7 at 65°.

I.	KCl, vol. in solution	26·5
II.	... ...	26·8
III.	... ...	27·2
	Mean . .	26·8

The whole of an equivalent thrown into turpentine (the salt having been decrepitated) increased 39·6, and 39·3 in two experiments. Half an equivalent, 37·35 grains, caused a rise in the stem of 19·6 in two experiments.

				Sp. gr.
I.	KCl, vol. of salt	39·6	...	1·887
II.	... ...	39·3	...	1·900
III.	... ...	39·2	...	1·905
IV.	... ...	39·2	...	1·905
	Mean . .	39·3	...	1·900

Chloride of Ammonium, $NH_4Cl = 53·66$.—Half an equivalent, 26·83 grains, dissolved in 1000 grains of water with an increase of 17·5 at a temperature of 60°; in two other experiments at 63°, the increase was 18·0.

I.	NH_4Cl, vol. in solution	35·0
II.	... ...	36·0
III.	... ...	36·0
	Mean . .	35·7

Our experiments on the specific gravity of this salt gave 1·578 as an uniform result, indicating a volume of 34·0.

Bromide of Potassium, KBr = 117·6.—The fourth part of an equivalent, 29·4 grains, on being dissolved in water at 49°, gave in two experiments an increase of 7·2; which gives for the volume of the salt in solution 28·8. The same quantity of salt, immersed in turpentine at 63°, caused an increase of 11·0 in two experiments.

			Sp. gr.
KBr, vol. of salt	44·0	...	2·672

Iodide of Potassium, KI = 165·82.—This salt was decrepitated, and on dissolving 41·5 grains gave an increase of 11·0 at 57°; a second experiment with 83 grains gave an increase of 22·0 at 55°.

I.	KI, vol. in solution	44
II.	... ...	44
	Mean . .	44

On projecting 41·45 grains of this salt, previously decrepitated, into turpentine, an increase of 13·6 and 13·5 was produced in two successive experiments.

			Sp. gr.
I.	KI, vol. of salt	54·4 ...	3·048
II.	... ...	54·0 ...	3·070
	Mean . .	54·2 ...	3·059

Chloride of Sodium, NaCl = 58·78.—The whole of an equivalent of this salt, previously decrepitated, dissolved in 1000 grains of water at 60° with a rise of 18·0; and in a second experiment of 18·2; in a third experiment 118 grains of salt were dissolved in 1000 grains of water at 62° with an increase of 38·0.

I.	NaCl, vol. in solution	18·0
II.	... ...	18·2
III.	... ...	18·9
	Mean . .	18·3

80 grains of salt were treated as described (page 405), in the mercurial volumenometer, and the empty part of the tube, after the restoration of the mercury, showed a volume of 40·0. The same quantity thrown into alcohol previously saturated with it, gave an increase of 39·5. The whole of an equivalent, 58·78 grains, thrown into a saturated solution, caused an increase of 29·3.

			Sp. gr.
I.	NaCl, vol. of salt	29·4 ...	2·000
II.	... ...	29·0 ...	2·026
III.	... ...	29·3 ...	2·006
	Mean . .	29·23 ...	2·011

Bromide of Sodium, NaBr + 3HO = 128·70.—On dissolving 25·7 grains of this salt in water, an increase of 9·2 was occasioned in two experiments at a temperature of 53°.

I. II. NaBr + 3HO, vol. in solution 46

The same quantity of salt put into turpentine caused an increase of 11.

NaBr + 3HO, vol. of salt 55 ... 2·340

Chloride of Barium, BaCl + 2HO = 122·83.—30·7 grains dissolved in 1000 grains of water, increased 7·0 at a temperature of 58°; a second experiment, in which 20 grains of the salt were dissolved, gave an increase of 4·5.

I.	BaCl + 2HO vol. in solution	28·0
II.	... ...	27·6
	Mean . .	27·8

The fourth of an equivalent, 30·7 grains, being immersed in a saturated solution, gave an increase of 9·7 at a temperature of 60°; and the same quantity in two other experiments gave an increase of 9·8.

				Sp. gr.
I.	Ba Cl + 2HO	vol. of salt	38·8 ...	3·166
II.	...	...	39·2 ...	3·133
III.	...	...	39·2 ...	3·133
		Mean . .	39·07 ...	3·144

Perchloride of Mercury, Hg Cl = 136·9.—The fourth of an equivalent, 34·2 grains, of corrosive sublimate, on being dissolved in 1000 grains of water, gave an increase of 4·6 at a temperature of 62°; a second experiment with the same quantity was attended with the same result.

I. II. Hg Cl, vol. in solution 18·4

Half an equivalent (68·45 grains), thrown into a saturated solution of the salt, caused an increase of 11·0 at a temperature of 56°.

			Sp. gr.
I.	Hg Cl.	vol. of salt 22 ...	6·223

Chloride of Hydrogen, HCl = 36·47.—It was of interest to ascertain the volume of hydrochloric acid, in order to compare it with the other chlorides of the magnesian metals when dissolved in water. It was natural to expect that the volume of muriatic acid in dilute solutions would be different from that possessed by it in its concentrated state; and therefore the following experiments must be viewed in this light. Peligot's salt, the bichromate of the chloride of potassium, on dissolving in water, was decomposed into bichromate of potash and muriatic acid, and the volume of the latter was obtained by deducting that due to the former salt and adding the volume of water. The fourth part of an equivalent of this salt, 44·75 grains, dissolved in 1000 grains of water with an increase of 13·5 at 65°; and of 13·6 in another experiment at 68°. This result gives for the whole volume of the salt when dissolved 54·0 and 54·4, from which must be deducted 45·0 for the volume of bichromate of potash, and 9 must be added on account of the equivalent of water.

I.	Muriatic acid, in dilute solutions		18·0
II.	...	... ...	18·4
		Mean . .	18·2

Chloride of Copper, Cu Cl + 2HO = 85·18.—Half an equivalent, 42·6 grains, was dissolved in 1000 grains of water with an increase of 13·4 at a temperature of 60°; on a second experiment, 47 grains occasioned an increase of 14·0 at a temperature of 58°.

I.	CuCl + 2HO,	vol. in solution	26·8
II.	...	...	25·4
		Mean . .	26·1

Half an equivalent, 42·6 grains, being immersed in a saturated solution at 62°, caused an increase of 17·0; a second experiment with the same quantity of salt gave an increase of 16·6.

			Sp. gr.
I.	CuCl + 2HO, vol. of salt	33·2 ...	2·566
II.	... ...	34·0 ...	2·505
	Mean . .	33·6 ...	2·535

Chloride of Copper and Ammonium, $CuCl + NH_4Cl + 2HO$ = 138·84.—34·7 grains of this salt, being dissolved in 1000 grains of water, gave an increase of 15·5 in the first experiment and of 15·4 in the second, both at a temperature of 68°.

I.	$CuCl + NH_4Cl + 2HO$, vol. in solution	62·0
II.	... ...	61·6
	Mean . .	61·8

32·46 grains, thrown into a saturated solution, caused an increase of 16·1 in two experiments at a temperature of 60°, and a repetition of the experiment confirmed this result.

Chloride of copper and ammonium, vol. of salt 68·8 ... 2·018

Chloride of Copper and Potassium, CuCl + KCl + 2HO = 159·88.—34·7 grains of this salt, being dissolved in 1000 grains of water, caused an increase of 11·5 at 62°.

CuCl + KCl + 2HO, vol. in solution 53·0

The same quantity (34·7 grains), thrown into a saturated solution, caused an increase of 14·3.

CuCl + KCl + 2HO, vol of salt 65·9 ... 2·426

Chloride of Tin, SnCl + 3HO = 121·39.—One-fourth of an equivalent (30·35 grains) was dissolved in 1000 grains of water, acidulated with muriatic acid, with an increase of 9·0 at a temperature of 60°; a second experiment, with the same quantity of salt and at the same temperature, gave an increase of 9·2.

I.	SnCl + 3HO, vol. in solution	36·0
II.	... ...	36·8
	Mean . .	36·4

The same quantity, 30·35 grains, of the salt being immersed in a saturated solution, yielded an increase of 11·0, the temperature being 60°; and exactly the same result attended the repetition of the experiment.

		Sp. gr.
SnCl + 3HO, vol. of salt	44·0 ...	2·759

Chloride of Tin and Ammonium, $SnCl + NH_4Cl + 3HO$ = 175·05.—On dissolving 44 grains of this salt in 1000 grains of water, the increase was 18·3 at a temperature of 60°; a

second experiment with the same quantity and at the same temperature, gave an increase of 18·5.

I.	Chloride of tin and ammonium, vol. in solution	72·7
II.	... ...	73·5
	Mean . .	73·1

On immersing 43·76 grains of the salt in a saturated solution, an increase of 20·8 was obtained at a temperature of 60°, which gives 83·2 as the volume of the equivalent, and 2·104 as the specific gravity of the salt.

Chloride of Tin and Potassium, $SnCl + KCl + 3HO = 196{\cdot}09$. —On dissolving 24·3 grains of the salt in 1000 grains of water, an increase of 8·0 was obtained at a temperature of 60°; and 48·5 grains, dissolved in the same quantity of water, gave an increase of 15·5.

I.	Chloride of tin and potassium, vol. in solution	64·5
II.	... ...	62·7
	Mean . .	63·6

On throwing the fourth part of an equivalent, 49 grains, into a saturated solution, an increase of 19·5 was obtained at a temperature of 54°.

		Sp. gr.
$SnCl + KCl + 3HO$, vol. of salt	78·0 ...	2·514

A. *Chloride of Mercury and Ammonium*, $HgCl + NH_4Cl + HO = 199{\cdot}8$.—On dissolving 49·95 grains of this salt in 1000 grains of water, an increase was obtained of 16·0, and in a second experiment of 16·2, the temperature being about 60° in both cases.

I. A.	Chloride of mercury and ammonium, vol. in sol.	64·0
II.	... ...	64·8
	Mean . .	64·4

The same quantity of salt, thrown into a saturated solution at 60°, occasioned an increase of 17·0 in two experiments, which makes the volume of the equivalent 68·0, and the specific gravity 2·938.

B. *Chloride of Mercury and Ammonium*, $NH_4Cl + 2HgCl + HO = 336{\cdot}4$.—On dissolving 42 grains of this salt in 1000 grains of water, an increase of 10·1 was occasioned in two experiments at 54°, and of 10·2 in a third experiment at 60°.

I. II.	$NH_4Cl + 2HgCl + HO$, vol. in solution	80·9
III.	... ...	81·6
	Mean . .	81·2

42 grains, or one-eighth of an equivalent, thrown into a saturated solution of the salt, caused a rise in the stem of 11 in two experiments.

			Sp. gr.
I. II. B.	Chloride of mercury and ammonium, vol. of salt .	88·0 ...	3·822.

Chloride of Mercury and Potassium, KCl + 2HgCl + 2HO = 366·5.—The eighth part of an equivalent, 45·8 grains, being dissolved in 1000 grains of water, caused in two experiments an increase of 10·1 at a temperature of 53°.

I. II.	Chloride of mercury and potassium, vol. in solution	80·8.

The same quantity of salt, 45·8 grains, thrown into a saturated solution, caused an increase of 12·0 in one experiment and of 12·4 in two other trials, the temperature in all the cases being 58°.

			Sp. gr.
I.	Chloride of mercury and potassium, vol. of salt	96·0 ...	3·818
II.	... ...	99·2 ...	3·694
III.	... ...	99·2 ...	3·694
	Mean . .	98·1 ...	3·735

Chloride of Mercury and Sodium, NaCl + 2HgCl + 4HO =368·5.—On dissolving 46·06 grains of this salt in 1000 grains of water, the increase was 12·4 at 63°. This gives for the equivalent a volume of 99·2, or 11 equivalents. The same quantity of salt thrown into turpentine produced an increase of 15·3, which gives for the equivalent 122·4, and for the specific gravity 3·011.

A careful consideration of the previous experiments shows that there are two distinct classes of chlorides, &c. The first of these is placed in Table IX., and possesses 11 as the divisor of the solid.

TABLE IX.

Designation.			Vol. in solution.			Volume of solid.				
Name.	Formula.	Atomic weight.	Volume by experiment.	9, taken as unity.	Volume by theory.	Volume by experiment.	11, taken as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Bromide of potassium .	K Br	117·6	28·8	3	27	44·0	4	44	2·672	2·672
Chloride of ammonium.	NH_4 Cl	53·66	35·7	4	36	34·0	3	33	1·626	1·578
Iodide of potassium ...	K I	165·82	44·0	5	45	54·2	5	55	3·015	3·059
Bromide of sodium ...	Na Br+3HO	128·70	46·0	5	45	55·0	5	55	2·340	2·340
Chloride of mercury ...	Hg Cl	136·9	18·4	2	18	22·0	2	22	6·223	6·223
Chloride of hydrogen...	H Cl	36·47	18·2	2	18	.....	...	...	.....	.....
Chloride of copper.....	Cu Cl+2HO	85·18	26·1	3	27	33·6	3	33	2·581	2·534
Chloride of tin	Sn Cl+3HO	121·39	36·4	4	36	44·0	4	44	2·759	2·759
Chloride of mercury and sodium	2Hg Cl + Na Cl +4HO	368·5	99·2	11	99	122·4	11	121	3·045	3·011

In the second class (Table IX. A.) the primitive volume is 9·8, or, as in the case of the double chlorides of tin, the metallic salt enters into combination with the volume 11; while NH_4Cl remains a multiple of 9·8. It is interesting to observe that NH_4Cl affects in combination as a solid the same number of volumes which it has as a liquid.

TABLE IX. A.—Showing the Volumes in solution and in the solid state of certain Chlorides.

Designation.			Vol. in solution.			Volume of salt.				
Name.	Formula.	Atomic weight.	Volume by experiment.	9, or volume of water as unity.	Volume by theory.	Volume of salt by experiment.	9·8, or volume of ice as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Chloride of potassium .	K Cl	74·7	26·8	3	27	39·3	4	39·2	1·905	1·900
Chloride of sodium.....	Na Cl	58·78	18·3	2	18	29·2	3	29·4	2·000	2·011
Chloride of barium ...	Ba Cl+2HO	122·83	27·8	3	27	39·07	4	39·2	3·133	3·144
Chloride of copper and potassium	Cu Cl+KCl+2HO	159·88	53·0	6	54	65·9	7	68·6	2·331	2·426
Chloride of copper and ammonium ...	Cu Cl + NH_4 Cl +2HO	138·84	61·8	7	63	68·8	7	68·6	2·024	2·018
Chloride of tin and ammonium	Sn Cl + NH_4 Cl +3HO	175·05	73·1	8	72	83·2	8	83·2	2·104	2·104
Chloride of tin and potassium	Sn Cl+KCl+3HO	196·09	63·6	7	63	78·0	8	78·4	2·501	2·514
A. Chloride of mercury and ammonium	Hg Cl + NH_4 Cl +HO	199·8	64·4	7	63	68	7	68·6	2·912	2·938
B. Chloride of mercury and ammonium	2Hg Cl+NH_4 Cl +HO	336·4	81·2	9	81	88	9	88·2	3·814	3·822
Chloride of mercury and potassium.....	2Hg Cl + KCl +2HO	366·5	80·8	9	81	98·1	10	98·0	3·739	3·736

The results of the experiments detailed in this section afford strong proofs of the law of multiple proportions, and exhibit at the same time that remarkable alteration of the divisor of the solid volumes which we have already noticed so frequently. Thus, while many of the chlorides and bromides are multiples of 11, we have decided exceptions in chlorides of potassium and sodium, which possess for their divisor the volume of ice, viz. 9·8; and this reappears in the double salts.

It is impossible, however, not to see that these results are somewhat singular, for in the double salts the chloride of potassium forces the double salt with which it is associated to assume the multiples of 9·8, and then exhibits its natural isomorphous relation to chloride of ammonium, which *per se* it did not possess. Chloride of ammonium, anomalous, in being a multiple of 11 in the solid state, assumes four volumes,

multiples of 9·8, in the double chlorides, and then presents the same number for its solid volume as chloride of potassium. The isomorphism of potassium and sodium is so entirely hypothetical, that it will not excite surprise to find the volumes of the chlorides so different. We were less prepared to detect the difference between iodide and chloride of potassium; but have confirmed it by an examination of iodide of ammonium, 50 grains of which dissolved in 1000 of water with an increase of 18·7, which gives $\frac{54{\cdot}1}{9}$ = six volumes for the equivalent, a result confirmatory of our determination of five volumes for iodide of potassium; the increase of one volume being in conformity with the usual behaviour of ammoniacal salts. We shall return to the consideration of the chlorides in a future section.

Section V.

Chromates.

The chromates present a class of salts which offer some peculiarities with regard to their volumes, in elucidating which we had occasion to repeat our experiments very often, and, therefore, give the mean of the results, instead of taking up unnecessary space in the Transactions of the Society by describing each experiment individually.

Chromic Acid, CrO_3=52·19.—The chromic acid used in our experiments was obtained by adding sulphuric acid to bichromate of potash. It was in beautiful distinct crystals of nearly a quarter of an inch in length, being the finest and purest specimen which we have obtained in many preparations of this acid.

The half of an equivalent, 26·09 grains, dissolved in 1000 of water with an increase of 9·0 at 72°; this gives 18·0 as the volume of chromic acid in solution.

The same quantity of acid, thrown into the solution from which it had crystallized, gave an increase of 9·7 and 9·8 in two experiments.

I. Chromic acid, volume	19·4	...	2·690
II.	19·6	...	2·663
Mean . .	19·5	...	2·676

Yellow Chromate of Potash, KO, CrO_3=99·50.—On dissolving 50 grains of this salt in 1000 grains of water, the increase was 9·0 at a temperature of 58°; this gives 17·9 as the volume of the equivalent in solution.

The mean result of *ten* experiments, on immersing 49·75

grains in turpentine, was an increase of 18·55, which gives 37·1 for the volume of the equivalent, and 2·682 as the specific gravity of the salt.

Sesquichromate of Potash, $2KO, 3CrO_3 = 251·09$.—This salt, which will be described in a future communication by one of us, is obtained by boiling a solution of bichromate of potash with an excess of finely pounded litharge. The oxide of lead removes only one-fourth of the chromic acid of the bichromate, and the solution on cooling deposits the sesquichromate in flattened prisms of a paler but more resplendent colour than the bichromate of potash. On dissolving the fourth part of an equivalent, 62·77 grains, in 1000 grains of water, the increase in four experiments at 58° was exactly 18·0; this gives 72·0 as the volume of the equivalent in solution.

The mean of six experiments, placing the fourth of an equivalent, 62·77 grains, in turpentine, was an increase of 23·7, which gives 94·8 as the volume of the equivalent, and 2·648 as the specific gravity of the salt.

Bichromate of Potash, $KO, 2CrO_3 = 151·70$.—On dissolving 76 grains of this salt in 1000 grains of water, an increase of 22·5 and 23·0 were obtained in two experiments at 60° and 65°.

I.	$KO, 2CrO_3$, vol. in solution	44·9
II.	... ...	45·8
	Mean . .	45·3

Half an equivalent of the salt, 75·84 grains, immersed in turpentine, gave an increase, the mean of *ten* experiments, of 28·9, which gives 57·8 as the volume of an equivalent, and 2·624 as the specific gravity of the salt.

Terchromate of Potash, $KO, 3CrO_3 = 203·92$.—This salt was obtained by mixing a solution of bichromate of potash with nitric acid and crystallizing. On dissolving 51 grains of the salt in 1000 grains of water, an increase was occasioned of 18·0 at 60°; this gives 71·9 as the volume of the equivalent in solution.

On immersing 50·98 grains in turpentine, the increase was 19·3 in two experiments, and 19·0 in a third trial.

I.	$KO, 3CrO_3$, vol. of salt	77·2	...	2·641
II.	... ...	77·2	...	2·641
III.	... ...	76·0	...	2·683
	Mean . .	76·8	...	2·655

Bichromate of Chloride of Potassium, $KCl + 2CrO_3 = 179·08$.—The fourth part of an equivalent, 44·77 grains, being

dissolved in 1000 grains measure of a dilute solution of muriatic acid, gave an increase of 15·7 in two experiments at 57°; this result makes the volume of an equivalent in solution 62·8.

The mean of various experiments on this salt gave an increase of 18·15 on immersing the above quantity of salt in turpentine, which yields 72·6 as the volume of the equivalent, and 2·466 as the specific gravity of the salt.

The results now described show that the chromates form a group different from the classes of salts hitherto given.

TABLE X.—Showing the Volumes occupied by certain Chromates.

Designation.			Volume of salt in solution.			Volume of salt.	
Name.	Formula.	Atomic weight.	Volume in solution by experiment.	9, taken as unity.	Volume by theory.	Volume of salt.	Specific gravity.
Chromic acid	CrO_3	52·19	18·0	2	18·0	19·5	2·676
Chromate of potash	KO, CrO_3	99·50	17·9	2	18·0	37·1	2·682
Sesquichromate of potash.	$2KO, 3CrO_3$	251·07	72·0	8	72·0	94·8	2·648
Bichromate of potash.....	$KO, 2CrO_3$	151·70	45·3	5	45	57·8	2·624
Terchromate of potash ...	$KO, 3CrO_3$	203·92	71·9	8	72	76·8	2·655
Bichromate of chloride of potassium	$KCl + 2CrO_3$	179·08	62·8	7	63	72·6	2·466

An inspection of the previous table will show clearly that the chromates differ from the salts described in the former sections. In the volumes in solution there is no difference; they are multiples of 9, and follow the usual law of the sum of the volumes, being made up of the volumes of the constituents of the salt. Chromate of potash possesses two volumes in solution, exactly as is the case with its analogue sulphate of potash. The latter salt affects three volumes in the solid state, and so naturally should chromate of potash. In bichromate of potash we see these three volumes appearing in solution, united to two volumes possessed by the chromic acid attached to the chromate of potash; in sesquichromate of potash they again reappear, and so also in terchromate of potash. The fact that the number of volumes possessed in the solid state by the lowest member of a series of salts passes over into the higher members when in solution, finds examples in the carbonates and oxalates, and is not peculiar to the chromates.

The solid volumes of the chromates possess decided peculiarities, being neither multiples of 11 nor of 9·8. Chromic acid

itself is obviously twice the volume of ice, $9{\cdot}8 \times 2 = 19{\cdot}6$, the experimental number being 19·5. But all the other salts in this group refuse to arrange themselves under either of the heads which we have found to explain most of the salts in the previous sections. In an exception of this kind we are entitled to make an assumption which will in all probability be near the truth, if by means of it we can bring into one uniform system a whole group of anomalous salts. Sesquichromate of potash is of great importance in the history of the chromates, from its frequent occurrence, although hitherto it has been altogether neglected by chemists. Chromic acid is actually able to displace sulphuric acid from sulphate of potash, in order to gratify its love for the potash in the peculiar condition of the sesquichromate. In numerous instances of decomposition, as will be pointed out by one of us in another paper, this sesquichromate appears. The sesquichromate is not formed readily, if indeed it is ever formed, by crystallizing chromate of potash with chromic acid in the proportion of sesquichromate, the result being bichromate of potash and chromate of potash, which crystallize separately. Here then is a remarkable point in the constitution of the chromates, which can only be explained by supposing that sesquichromate of potash contains a double atom of chromate of potash united to one of chromic acid. The decomposition of bichromate of potash by oxide of lead necessarily implies that its atom should also be doubled; $2KO, 3CrO_3 + CrO_3$ boiled with litharge, gives $2KO, 3CrO_3 + PbO, CrO_3$.

We have found the volume of KO, CrO_3 to be 37·1, not 33·0, as in the case of sulphate of potash. Karsten obtained the specific gravity 2·640, which gives the volume 37·6; and Thomson states the specific gravity to be 2·612, which gives the volume 38·1; the mean of all these experiments is 37·6, which, multiplied by 2, for the reasons already stated, gives as the volume of $2(KO, CrO_3)$, 75·2. The natural volume of chromate of potash, deduced from its analogy to sulphate of potash, would be 11×3, or on the double atom $11 \times 6 = 66$. Now, the assumption we make to explain this class of salts is, that the double atom of chromate of potash enjoys its anomalous character by adding to its natural volume the volume of ice, thus $66{\cdot}0 + 9{\cdot}8 = 75{\cdot}8$, which is not very far from the volume ascertained by experiment. This assumption of a volume of ice, in addition to other volumes of 11, has been shown to exist in the magnesian sulphates, and therefore its hypothetical existence in the chromates is by no means extravagant. Sesquichromate of potash must then be the double chromate of potash united to an equivalent of chromic acid, $75{\cdot}8 + 19{\cdot}6$

=95·4, which is not very far from 94·8, the volume determined by experiment. Bichromate of potash would consist of a double atom of chromate of potash and 2 of chromic acid, or 75·8 + 39·2 = 115·0, which agrees pretty closely with the experimental determination of 115·6; and terchromate of potash, in like manner, is 1 atom of double chromate of potash with 4 of chromic acid, or 75·8 + 78·4 = 154·2, which is almost exactly the same as 154·4, found in the two consecutive experiments, and not far distant from 153·6, the mean of the three experiments.

This view receives confirmation from the volume of Peligot's salt, which certainly consists of the volume of KCl, when in combination, added to that of 2 atoms of chromic acid, 33·0 + 39·2 = 72·2, a number very close to the experimental result 72·6. It is quite true that we have made a gratuitous assumption at the outset of our explanation; but it is not surprising to find an unusual law prevailing in a class of salts so anomalous as the chromates. When the experimental numbers, and those calculated on the assumption, are so near as we have shown them to be, there is, we think, a good argument for the truth of the hypothesis.

TABLE X.a.

Name.	Formula.	Volume by experiment.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Chromic acid	CrO_3	19·5	19·6	2·663	2·676
Chromate of potash, doubled	$(2KO,2CrO_3)$	75·2	75·8	2·627	2·646
Sesquichromate of potash	$(2KO,2CrO_3)+CrO_3$	94·8	95·4	2·658	2·648
Bichromate of potash ...	$(2KO,2CrO_3)+2CrO_3$	115·6	115·0	2·638	2·624
Terchromate of potash ...	$(2KO,2CrO_3)+4CrO_3$	154·4	154·2	2·644	2·641
Bichromate of chloride of potassium	$KCl+2CrO_3$	72·6	72·2	2·480	2·466

A singular result obtained in the examination of the anhydrous double sulphates seems to be explained by the behaviour of the chromates. We found sulphate of copper and potash and sulphate of magnesia and potash to affect a volume of 59·8 instead of 55·0, and we ascertained, by many experiments, that this high number was not due to an error of observation. Now, if we suppose the KO, SO_3 in these salts to behave like KO, CrO_3 in assuming one volume of ice on the double atom, then $2KO, SO_3 = 75·8 + 2MO, SO_3 = 44·0 = \frac{119·8}{2} = 59·9$,

a number almost identical with the experimental result. On this view, then, anhydrous double sulphates are constituted on the type of red chromate of potash, the *two volumes* of CrO_3 being replaced by the *two volumes* of MO, SO_3. Anhydrous alum was found to have a volume of 116·4 instead of 111·4, but would be reconciled with theory, if we supposed it to contain the peculiar KO, SO_3 analogous to KO, CrO_3; in this case the theoretical volume would be 116·3.

Section VI.

Carbonates.

Carbonate of Potash, $KO, CO_2 = 69·4$.—On dissolving 34·7 grains of carbonate of potash in 1000 grains of water, the increase was 4·6 at 62°; the atomic volume in solution is therefore 9·2. The same quantity of salt thrown into turpentine caused, in various experiments, an increase of 16·5; this makes the volume of the equivalent 33·0, and the specific gravity of the salt 2·103.

Bicarbonate of Potash, $KO, HO, 2CO_2 = 100·6$.—The fourth part of an equivalent (25·1 grains) dissolved in 1000 grains of water, at 61°, with an increase of 8·9, and in another experiment of 9·0. The mean of these results, 8·95, gives as the volume of the equivalent in solution, 35·8. The same quantity of salt, thrown into turpentine, gave an increase of 12·0, in various experiments, which gives for the specific volume of the salt 48·0, and for its specific gravity 2·092. As this salt was one of the very few substances used in this inquiry not prepared by ourselves, we take the mean of our own result, and the only other recorded specific gravity of which we are aware, viz. that by Gmelin, 2·012, and adopt 49·0 as the correct volume, and 2·052 as the specific gravity.

Bicarbonate of Ammonia, $HO, NH_4O, 2CO_2 = 79·3$.—This salt was made by exposing the carbonate of the shops to the air until it ceased to emit smell, and then crystallizing the remainder. On dissolving 19·82 grains, the fourth of an equivalent, in 1000 grains of water, the increase was 9·0 at 55°, and 9·4 in another experiment at 62°. The mean result gives 36·8 as the volume of the salt in solution.

On immersing 19·82 grains of the salt in turpentine, an increase of 12·5 was effected, which gives as the volume of the salt 50·0, and for its specific gravity 1·586.

Bicarbonate of Soda, $NaO, HO, 2CO_2 = 84·64$.—On dissolving 42·32 grains of this salt in 1000 grains of water at 67°, an increase of 9·0 was obtained; this gives for the volume of an equivalent in solution 18·0. On immersing the same quantity of salt in turpentine, the increase was 19·4 and 19·2 in two experiments.

I.	$NaO, HO, 2CO_2$, vol. of salt	38·8	...	2·181
II.	... ...	38·4	...	2·204
	Mean . .	38·6	...	2·192

Although we have examined other carbonates, we purposely avoid bringing them into the present paper, because they involve considerations upon which we are at present engaged in minute study, and do not wish to hazard without sufficient proof. We subjoin the few carbonates here examined in a tabular form.

TABLE XI.—Showing the Volumes occupied by the Alkaline Carbonates.

Designation.			Vol. in solution.			Volume of salt.	
Name.	Formula.	Atomic Weight.	Volume in solution.	9, taken as unity.	Volume by theory.	Volume of salt by experiment.	Specific gravity by experiment.
Carbonate of potash	KO, CO_2	69·4	9·2	1	9	33·0	2·103
Carbonate of soda	NaO, CO_2	53·47	...	...	...	22·0	2·427
Bicarbonate of potash ...	$HO, KO, 2CO_2$	100·6	35·8	4	36	49·0	2·052
Bicarbonate of soda	$HO, NaO, 2CO_2$	84·64	18·0	2	18	38·6	2·192
Bicarbonate of ammonia .	$HO, NH_4O, 2CO_2$	79·3	36·8	4	36	50·0	1·586

The results shown in this table will appear perplexing, unless the facts already observed in the previous sections be borne in mind. We find in carbonate of potash an astonishing difference between the liquid and the solid volume; and this is still more marked in the case of carbonate of soda, which ceases to occupy volume in solution. Both of these salts have 11 as the divisors of their solid volume, KO, CO_2 affecting three, and NaO, CO_2 two volumes. In the last section we saw that the three volumes possessed by chromate of potash in its solid state passed over into bichromate of potash; and in bicarbonates of potash and ammonia we observe the same circumstance, except that the volumes change from multiples of 11 to multiples of 9·8, and in solution are one less than in the state of a salt. It is probably owing to this circumstance that we do not in this case observe the usual increase of one volume in the ammoniacal over the corresponding salt of potash. The bicarbonates of potash, soda and ammonia are probably multiples of 9·8, or the volume of ice.

	Vol. by experiment.	Vol. by theory.
Bicarbonate of potash	49·0 .. 2·052	$9·8 \times 5 = 49·0$ .. 2·052
... ammonia	50·0 .. 1·586	$9·8 \times 5 = 49·0$ .. 1·618
... soda .	38·6 .. 2·192	$9·8 \times 4 = 39·2$ .. 2·159

Section VII.

Oxalates.

The oxalates offered an interesting group of salts for examination, especially on account of the accurate determination of their composition and hydration by Graham.

Oxalate of Water, $HO, C_2O_3 + 2HO = 63{\cdot}26$.—32 grains of oxalic acid, dissolved in 1000 grains of water, caused an increase of 18·5 at a temperature of 55°; the same quantity, being subjected to a second experiment, caused an increase of 19; and a third experiment, in which 21 grains were dissolved in 9½ ounces of water, occasioned an increase of 12 at 40°.

I.	$HO, C_2O_3 + 2HO$, vol. in solution	36·5
II.	... ...	37·5
III.	... ...	36·0
	Mean . .	36·6

A whole equivalent thrown into turpentine caused, in various experiments, an increase of 39·0, which gives for its specific gravity 1·622. Richter states the specific gravity to be 1·507; but it is impossible that he can have operated upon a pure specimen, as we have repeated the experiments upon this acid very frequently.

Oxalate of Potash, $KO, C_2O_3 + HO = 92{\cdot}39$.—A quantity of salt, 42·5 grains, being dissolved in 1000 grains of water, gave an increase of 13·0; and the same result attended a repetition of the experiment, the temperature in both cases being at 60°.

$KO, C_2O_3 + HO$, vol. in solution 28·2

46·2 grains of the same salt, being put into a saturated solution, caused a rise in the stem of 22·0; a repetition of the experiment with the same quantity gave the increase 21·9, the temperature in both cases being 61°.

				Sp. gr.
I.	$KO, C_2O_3 + HO$, vol. of salt	44·0	...	2·100
II.	... ...	43·8	...	2·109
	Mean . .	43·9	...	2·104

Oxalate of Ammonia, $NH_4O, C_2O_3 + HO = 71{\cdot}43$.—Half an equivalent of this salt (35·71 grains) was dissolved in 1000 grains of water with an increase of 18·0 at a temperature of 55°; and a repetition of the experiment with the same quantities and at the same temperature, gave exactly the same result.

I. II. $NH_4O, C_2O_3 + HO$, vol. in solution 36

35·71 grains, being immersed in a saturated solution, gave in the first experiment an increase of 24·5, in the second of 24·4; the first experiment being at 48°, the second at 50°.

			Sp. gr.
I. $NH_4O, C_2O_3 + HO$, vol. of salt	49·0	...	1·458
II.	48·8	...	1·464
Mean . .	48·9	...	1·461

Binoxalate of Potash, $KO, C_2O_3 + HO, C_2O_3 + 2HO$ = 146·63.—To determine the volume of this salt, 18·33 grains were dissolved in 1000 grains of water with a rise of 6·8 at a temperature of 57°; and the same result attended a repetition of the experiment; in a third experiment, 25 grains at the same temperature caused an increase of 9·0.

I. II. Binoxalate of potash, vol. in solution	54·4
III.	52·8
Mean . .	53·6

Half an equivalent of the salt (73·31 grains), being immersed in a saturated solution, caused an increase of 37·4 in the first experiment, and of 37·2 in the second, the temperature in both cases being 55°.

			Sp. gr.
I. Binoxalate of potash, vol. of salt	74·8	...	1·960
II.	74·4	...	1·971
Mean . .	74·6	...	1·965

Oxalate of Copper and Potash, $KO, C_2O_3 + CuO, C_2O_3 + 2HO$ = 177·25.—On account of the sparing solubility of this salt, 11·08 grains, or the sixteenth part of an equivalent, were dissolved in water, and caused an increase of 3·4 in two experiments at a temperature of 59°.

I. II. $KO, C_2O_3 + CuO, C_2O_3 + 2HO$, vol. in solution 54·4

The fourth of an equivalent (44·3 grains), placed in a saturated solution, caused an increase in one experiment of 19·5; in another of 18·9; and in a third of 19·7; all at a temperature varying from 54° to 57°.

			Sp. gr.
I. Oxalate of copper and potash, vol. of salt	78·0	...	2·272
II.	75·6	...	2·344
III.	78·8	...	2·249
Mean . .	77·5	...	2·288

Binoxalate of Ammonia, $NH_4O, C_2O_3 + HO, C_2O_3 + 2HO$ = 125·69.—31·42 grains of this salt, dissolved in 1000 grains of water, caused in the first experiment an increase of 18·0 at 60°; in the second, of 18·2 at 61°; in a third experiment, of

17·8 at 54°; in a fourth, 42 grains dissolved in 4100 grains of water increased 24·0 at 53°.

I.	Binoxalate of ammonia, vol. in solution	72·0
II.	... ...	72·8
III.	... ...	71·2
IV.	... ...	71·8
	Mean . .	71·9

The half of an equivalent (62·84 grains), being immersed in a saturated solution, caused an increase of 40·3 in two experiments, and of 40·0 in a third.

				Sp. gr.
I.	Binoxalate of ammonia, vol. of salt	80·6	...	1·559
II.	... ...	80·6	...	1·559
III.	... ...	80·0	...	1·571
	Mean . .	80·4	...	1·563

Oxalate of Copper and Ammonia, $NH_4O, C_2O_3 + CuO, C_2O_3 + 2HO = 156{\cdot}38$.—The solution of 18·3 grains gave an increase of 8·6 at 65°; this gives 73·3 as the volume of this salt when in solution.

On immersing 20 grains in turpentine, an increase of 10·4 was obtained, which gives for the volume of the equivalent 81·3, and for the specific gravity of the salt 1·923.

Quadroxalate of Potash, $KO, C_2O_3 + 3HO, C_2O_3 + 4HO = 255{\cdot}11$.—32·0 grains dissolved in water, gave an increase of 15·0 at 60°; and a second experiment, in which 16 grains were dissolved in 1000 grains of water, gave the increase of 7·2 at a temperature of 44°.

I.	Quadroxalate of potash, vol. in solution	119·4
II.	... ...	114·8
	Mean . .	117·1

63·8 grains, the fourth part of an equivalent, thrown into a saturated solution, caused a rise of 35·1 in two experiments.

				Sp. gr.
I. II.	Quadroxalate of potash, vol. of salt	140·4	...	1·817

Quadroxalate of Ammonia, $KO, C_2O_3 + 3HO, C_2O_3 + 4HO = 234{\cdot}15$.—On dissolving 20 grains of this salt in 3500 grains of water at 50°, the increase is 11·5, which gives 134·5 as the volume of the equivalent in solution.

58·5 grains of the salt, thrown into a saturated solution, caused in the first experiment an increase of 36·8, in the second of 36·9, both at a temperature of 62°.

				Sp. gr.
I.	Quadroxalate of ammonia, vol. of salt	147·2	...	1·591
II.	... ...	147·6	...	1·586
	Mean . .	147·4	...	1·589

The volumes of the oxalates can only be explained by an attentive consideration of the previous results. We have already seen numerous instances in which the primitive volumes 9·8 and 11·0 become mutually convertible; this is strikingly the case with the salts of the present section. Hydrated oxalic acid has a volume 9·8 × 4; oxalate of potash possesses the volume 11 × 3, and passes with this volume into the binoxalate and quadroxalate of potash, the oxalic acid in the binoxalate being associated as two volumes of ice, although the water of crystallization possesses the volume 11. Quadroxalate of potash is to be viewed as anhydrous binoxalate *plus* 2 equiv. hydrated oxalic acid, the latter having become 11 × 4 instead of 9·8 × 4. The same explanation applies to the binoxalate and quadroxalate of ammonia, the only difference being that anhydrous oxalate of ammonia, 9·8 × 4, takes the place of oxalate of potash. On these views the following table is constructed.

TABLE XII.—Showing the volumes occupied by certain Oxalates.

Designation.			Vol. in solution.			Volume in state of salt.				
Name.	Formula.	Atomic weight.	Volume in solution by experiment.	9, or volume of water as unity.	Volume by theory.	Volume by experiment.	11 and 9·8, taken as unity, as above described.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Oxalic acid	HO, C_2O_3+2HO	63·26	36·6	4	36	39·0	4	39·2	1·616	1·622
Oxalate of potash...	KO, C_2O_3+HO	92·39	28·2	3	27	43·9	4	44·0	2·100	2·104
Oxalate of ammonia	NH_4O, C_2O_3+HO	71·43	36·0	4	36	48·9	5	49·0	1·458	1·461
Binoxalate of potash.....	$KO, 2C_2O_3+3HO$	146·63	53·6	6	54	74·6	7	74·6	1·965	1·965
Binoxalate of ammonia.....	$NH_4O, 2C_2O_3+3HO$	125·67	71·9	8	72	80·4	8	80·8	1·555	1·563
Oxalate of copper and potash.....	$KO, C_2O_3 + CuO, C_2O_3 +2HO$	177·25	54·4	6	54	77·5	7	77·0	2·301	2·288
Oxalate of copper and ammonia...	$NH_4O, C_2O_3+CuO, C_2O_3 +2HO$	156·38	73·3	8	72	81·3	8	80·8	1·935	1·923
Quadroxalate of potash	$KO\,4C_2O_3+7HO$	255·11	117·1	13	117	140·4	13	140·6	1·814	1·817
Quadroxalate of ammonia	$NH_4O, 4C_2O_3+7HO$	234·15	134·5	15	135	147·4	14	146·8	1·595	1·589

The examination of the volumes occupied by the oxalates presents several points of great interest. The volume of oxalic acid itself is a multiple of the volume of ice, or 9·8 × 4.

Oxalate of potash in its solid state possesses four volumes, 11 × 4, but loses one volume on passing into solution, as usually is the case with neutral salts of potash. As one of

these volumes is due to its combined water, the proper number of volumes in anhydrous oxalate of potash is three, and these it carries into binoxalate of potash, which is therefore a simple combination of oxalate of potash and hydrated oxalic acid, the crystalline water of the latter having assumed the volume 11.

	In solution.		As a salt.
KO, C_2O_3	18	...	33·0
$HO, C_2O_3 + 2HO$ . . .	36	...	41·6
Binoxalate of potash . . .	54	...	74·6

The only difference between the volumes of this salt and those of its constituents, when uncombined, is that the crystalline water of the hydrated oxalic acid has assumed the volume 11. Quadroxalate of potash consists of anhydrous binoxalate of potash united to hydrated oxalic acid, as Graham has already announced in his researches on the oxalates. The three volumes affected by oxalate of potash in its solid state pass into solution with it in quadroxalate of potash, just as we saw in the case of chromate and bichromate of potash; and the attached oxalic acid affects 11×4 instead of $9{\cdot}8 \times 4$.

	In solution.		As a salt.
I. Anhydrous binoxalate of potash	45	...	52·6
II. Hydrated oxalic acid	72	...	88·0
Quadroxalate of potash . . .	117	...	140·6

The assumption of two volumes in solution above those of binoxalate of potash was already characteristic of binoxalate of ammonia, and the same increase is seen in the quadroxalate, showing clearly that that salt must contain its ammonia *quasi* binoxalate and not as oxalate of ammonia. It is very possible that the volumes in solution of quadroxalate of ammonia should be 14, instead of 15, but the temperature 31°, at which it comes out 14 volumes, is so low, that it is more natural to keep the volumes we have given in the table.

It is interesting to observe how closely oxalate of copper relates itself to oxalate of water.

	Volumes in solution.		Volumes as salt.
Oxalate of copper and potash .	6	...	7
... water and potash .	6	...	7
... copper and ammonia	8	...	8
... water and ammonia .	8	...	8

Thus, even in the apparently anomalous behaviour of binoxalate of ammonia, in assuming two volumes more than the corresponding salt of potash, we find oxalate of copper and ammonia imitating its example. The reason of their increase will be explained in the next section.

Section VIII.

Subsalts and Ammoniacal Salts.

The salts which we have hitherto examined have been those soluble in water, and having a constitution to a certain degree well-defined. We have now to consider the insoluble subsalts, and, in some cases, their neutral insoluble types, and also to ascertain how far the results thus obtained serve to throw light on the constitution of ammoniacal salts.

Subsulphate of Copper, $CuO, SO_3, 4HO + 3CuO = 234{\cdot}9$. —This well-known salt was made by adding ammonia to a solution of sulphate of copper. The fourth part of an equivalent, 58·7 grains, thrown into water, caused an increase of 19·1 and 19·0 in two successive experiments.

			Sp. gr.
I.	Subsulphate of copper, vol. of salt	76·4 ...	3·074
II.	... ...	76·0 ...	3·090
	Mean . .	76·2 ...	3·082

Subsulphate of Zinc, $ZnO, SO_3, 3ZnO, 4HO = 237{\cdot}3$.— This salt is apt to combine with more water than four atoms, but may be obtained with four by drying at 212°. On placing 29·66 grains, the eighth part of an equivalent, in turpentine, an increase of 9·5 was obtained; and on treating 22·8 in a similar manner, the rise in the stem was 7·3. Both of these experiments exactly agree in making—

		Sp. gr.
Subsulphate of zinc, vol. of salt	76·0 ...	3·122

Sulphate of Protoxide of Mercury, $Hg_2O, SO_3 = 251{\cdot}0$.— This salt was prepared in the usual way by digesting one part of mercury in $1\frac{1}{2}$ part of sulphuric acid. The fourth of an equivalent, 62·75 grains, thrown into turpentine, increased 8·3.

		Sp. gr.
Hg_2O, SO_3, vol. of salt	33·2 ...	7·560

Sulphate of Peroxide of Mercury, $HgO, SO_3 = 149{\cdot}6$.— The salt used in the experiment was prepared by heating five parts of sulphuric acid mixed with a little nitric acid, with four parts of mercury until the whole became a dry saline mass. On immersing 37·5 grains of the salt thus prepared in turpentine, an increase of 5·8 was obtained, which gives 23·1 for the volume of the equivalent, and 6·466 for the specific gravity of the salt.

Subsulphate of Mercury, $HgO, SO_3 + 2HgO = 368{\cdot}46$.— The last salt thrown into water and washed with warm water is converted into the beautiful yellow powder known as tur-

peth mineral. On throwing 57·4 grains of this salt thus prepared into water, an increase of 6·9 was obtained, which gives 44·3 as the volume of the equivalent, and 8·319 as the specific gravity of the salt.

Chromate of Lead, PbO, CrO_3 = 163·97.—On throwing 81·98 grains of the chromate of lead, previously well-dried, into turpentine, an increase of 14·5 was effected; this gives 29·0 as the volume of the equivalent, and 5·653 as the specific gravity of the salt.

Subchromate of Lead, PbO, CrO_3 + PbO = 275·7.—This salt was prepared by projecting chromate of lead into melted nitre, and afterwards washing out all soluble matter. On immersing 68·92 grains, the fourth part of an equivalent, an increase of 11·0 was obtained in two experiments. This gives 44·0 for the volume of the equivalent, and 6·266 as the specific gravity of the salt.

Sesquibasic Chromate of Lead, 2(PbO, CrO_3) + PbO = 439·67.—The mineral, melanchroit, is of the composition expressed by the above formula, and has a specific gravity of 5·75 according to Hermann; this gives the number 76·5 as the atomic volume of the compound.

Subnitrate of Copper, CuO, NO_5, HO, 2CuO = 182·17.—The fourth part of an equivalent, 45·54 grains, caused an increase of 16·5 in two experiments, and of 16·4 in a third.

					Sp. gr.
I.	CuO, NO_5, HO + 2CuO,	vol. of salt	66·0 ...		2·760
II.	...	...	66·0 ...		2·760
III.	...	...	65·6 ...		2·777
		Mean . .	65·87 ...		2·765

A. *Subnitrate of Bismuth*, BiO, NO_5, HO + 2BiO = 300·4.—This salt was prepared in the same manner as subnitrate of copper, viz. by heating the nitrate to 400° or 500°. The fourth part of an equivalent, 75·1 grains, thrown into water, caused, in various experiments, an increase of 16·5, which gives 66·0 as the atomic volume, and 4·551 as the specific gravity of the salt.

B. *Subnitrate of Bismuth*, BiO, NO_5 + 2BiO = 291·4.—This salt was prepared by adding nitrate of bismuth to a large quantity of water; the white powder which falls by this treatment, is composed, according to Phillips, of three equivalents of oxide of bismuth united to one of nitric acid. It is therefore the same salt as the one last described, deprived of its constitutional water. On immersing 72·85 grains of the salt in water, a rise in the stem of 13·9 was effected, and 36·42 grains treated in the same way gave an increase of 6·9.

				Sp. gr.
I.	$3BiO, NO_5$, vol. of salt	55·6	...	5·241
II.	... ...	55·2	...	5·279
	Mean . .	55·4	...	5·260

Subnitrate of Mercury, $HgO, NO_5 HO + 2HgO = 391·49$. —This salt was obtained in a yellow powder by adding the crystallized subnitrate of mercury to water, and washing it, according to the directions of Kane, with hot, but not boiling water. The fourth part of an equivalent, 97·87 grains, thrown into turpentine, caused an increase of 16·4, which gives 65·6 as the atomic volume of the salt, and 5·967 as the specific gravity.

Ammoniacal Sulphate of Copper, $CuO, SO_3 HO, + 2NH_3 = 123·0$.—This salt has already been described in a previous section; it had a volume of 54·0 or 9 × 6 in a state of solution, and of 68·6 or 9·8 × 7 in the solid state. The salt examined in that case was in fine large indigo blue crystals, and was prepared by ourselves. Another portion, made by Mr. Morson in small crystals, we found to possess a volume of 68·0 and specific gravity of 1·809. When this salt is heated it loses one equivalent of water and one of ammonia, being converted into a green powder, the formula of which is $CuO, SO_3 + NH_3$; 24·27 grains of this, thrown into turpentine, caused an increase of 9·8, which gives 39·2 as the volume of the equivalent, and 2·476 as the specific gravity of the salt. The latter salt on being moistened with water absorbs three equivalents, and therefore assumes the atomic weight of 124·07; the fourth part of which, 31·0 grains, thrown into turpentine, caused an increase of 15·9, making the atomic volume of $CuO, SO_3 + NH_3 + 3HO$, 63·6, and its specific gravity 1·950.

Ammonia-Sulphate of Zinc.—Kane describes several ammonia-sulphates of zinc, obtained by passing a stream of ammonia through a hot solution of sulphate of zinc, until the precipitate at first formed is redissolved. The solution thus obtained deposited transparent crystals in a few hours, but these effloresced so quickly after being dried, that we did not determine their specific gravity. The effloresced crystals have, according to Kane, the formula—

$$ZnO, SO_3 + 2\,NH_3 + 2\,HO = 132·8.$$

We fear, however, that we have not been successful in procuring this salt in its proper state, as the determination of its volume varied between 57·5 and 64·0, results so discordant, that it would not be safe to take their mean as a correct result. On heating this salt it loses water and ammonia, being

converted into $ZnO, SO_3 + NH_3$; 26·7 grains of which (the fourth of an equivalent), thrown into turpentine, caused an increase of 10·8, which gives 39·5 as the volume of the salt, and 2·479 for its specific gravity.

Ammonia-Sulphate of Mercury, $HgO, SO_3 + HgAd + 2HgO = 486·0$.—This salt, which Kane calls the Ammonia Turpeth, was prepared by heating turpeth mineral with ammonia until it became changed to a heavy white powder. The eighth part of an equivalent, 60·75 grains, immersed in water, caused an increase of 8·3 in two experiments; this makes the volume of the compound 66·4, and its specific weight 7·319.

Ammonia-Sulphate of Silver, $AgO, SO_3 + 2NH_3 = 190·86$. —This salt was obtained in the usual way, by dissolving sulphate of silver in ammonia and crystallizing. The first specimen tried was in small, indistinct crystals, in the second instance the crystals were large and well-defined. 25·62 grains gave an increase of 8·6, and 37·7 grains of the better specimen of salt gave the increase 13·2.

			Sp. gr.
I.	$AgO, SO_3 + 2NH_3$, vol. of salt	64·0 ...	2·979
II.	... ...	66·8 ...	2·857
	Mean . .	65·4 ...	2·918

Ammonia-Chromate of Silver, $AgO, CrO_3 + 2NH_3 = 202·8$. —This salt was obtained in fine large crystals, in the same manner as the last salt. On immersing 25·35 grains in turpentine, the increase was 8·3, and on treating 50·7 grains in the same way, the increase was 16·5.

			Sp. gr.
I.	$AgO, CrO_3 + 2NH_3$, vol. of salt	66·4 ...	3·054
II.	... ...	66·0 ...	3·073
	Mean . .	66·2 ...	3·063

Ammonia-Nitrate of Copper, $CuO, NO_5 + 2NH_3 = 128·4$. —On dissolving 64·2 grains, half an equivalent, in 1000 grains of water, the increase was 32·0 in two experiments at a temperature of 60°; this makes the atomic volume in solution 64·0. On putting the same quantity into turpentine, there was a rise in the stem, in three experiments, of 34·0, 34·0, and 34·8.

			Sp. gr.
I.	$CuO, NO_5 + 2NH_3$, vol. of salt	68·0 ...	1·888
II.	... ...	68·0 ...	1·888
III.	... ...	69·6 ...	1·845
	Mean . .	68·5 ...	1·874

Ammonia-Sub-Nitrate of Mercury, $HgO, NO_5 + 2HgO + NH_3 = 399·7$.—This salt was prepared by adding a dilute

solution of ammonia to nitrate of mercury, and was of a pure milk-white colour, as described by Kane. On throwing 40 grains of this compound into water, an increase of 6·7 was obtained; this gives a volume of 67·0 on the equivalent, and 5·970 as the specific gravity of the salt.

Chloride of Copper, $CuCl = 67{\cdot}18$.—The volume of hydrated chloride of copper was shown to be 33 or 3×11; but we have not yet examined the bulk occupied by the anhydrous chloride. The chloride was deprived of its water by a heat considerably below that of redness, in order to prevent the formation of any sub-chloride. On throwing 33·59 grains, or half an equivalent, into turpentine, the increase in two experiments was exactly 11·0, which gives 22·0 as the volume of the salt, and 3·054 as its specific gravity.

Ammonia-Chloride of Copper, $CuCl + 2NH_3 + HO = 110{\cdot}3$. —This salt was made by passing a stream of ammonia through a solution of chloride of copper until the precipitate formed had completely redissolved. The crystals, which deposited as the solution cooled, were dried in a receiver containing slaked lime, so as to prevent the carbonic acid of the atmosphere acting upon the ammonia; but in spite of this precaution the crystals had slightly effloresced on the surface. The effloresced matter was removed, and the pure crystals employed. 27·6 grains of them, when thrown into turpentine, produced in two experiments an increase of 16·5, making the volume of the salt 66·0, and its specific gravity 1·672. On dissolving the same quantity of salt, 27·6 grains, in 1000 grains of water, the rise was 15·9 at 62°, making the volume of the salt when in solution 63·6.

On exposing this salt to heat, water and ammonia are expelled, and a green powder remains, having the formula $CuCl + NH_3$. 21·07 grains of this salt thrown into turpentine produced an increase of 9·6, making the volume of the equivalent 38·4, and the specific gravity of the salt 2·194.

Subchloride of Copper, $Cu_2Cl = 98{\cdot}89$.—The subchloride used in the experiment was made by adding protochloride of tin to a solution of chloride of copper. During the desiccation of the salt it became slightly green, showing that a little chloride had been formed by the absorption of oxygen; but the change was so slight as probably not to interfere materially with the result; 42·2 grains, thrown into turpentine, caused an increase of 12·5, which gives 29·2 as the volume, and 3·376 as the specific gravity of the salt.

Subchloride of Mercury, $Hg_2Cl = 238{\cdot}33$.—The fourth part of an equivalent, 59·58 grains, thrown into turpentine, caused an increase of 8·3.

			Sp. gr.
Calomel, vol. of salt	33·2	...	7·178

Hassenfratz states the specific gravity to be 7·176, a result very near our own determination.

Subchloride and Amide of Mercury, $Hg_2Cl + Hg_2Ad = 458·1$.—The eighth part of an equivalent, 57·26 grains, thrown into water, caused an increase of 8·3 and 8·4 in two experiments.

				Sp. gr.
I.	Black compound of calomel	67·2	...	6·816
II.	... ...	66·4	...	6·899
	Mean . .	66·8	...	6·858

The salt used in the experiments was prepared in the usual way, by acting upon calomel with ammonia.

Chloride and Amide of Mercury, $HgCl + HgAd = 254·5$.—The excellent researches of Kane, so often alluded to, have shown that the above formula represents the composition of white precipitate. It must be dried by a pretty strong heat, to get rid of all its hygrometric water. On projecting 63·8 grains, the fourth of an equivalent, into water, an increase of 11·2 was obtained in two experiments; this gives 44·6 as the specific volume of the compound, and 5·700 as its specific gravity.

Basic Chloride and Amide of Mercury, $HgCl + HgAd + 2HgO = 473·3$.—This yellow compound was made in the usual way, by boiling white precipitate with water. On throwing 59·2 grains into water, the rise was 8·2 in one experiment, and 8·3 in another.

				Sp. gr.
I.	The above salt, volume	65·5	...	7·220
II.	... ...	66·3	...	7·132
	Mean . .	65·9	...	7·176

Table XIII.—Showing the Volumes occupied by certain Subsalts and Salts of Ammonia.

Designation.			Volume in solution.			Volume of salt.				
Name.	Formula.	Atomic weight.	Volume of salt in solution.	9, taken as unity.	Volume by theory.	Volume of salt by experiment.	11, taken as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Subsulphate of copper	$\left\{\begin{matrix}CuO, SO_3, 3CuO \\ +4HO\end{matrix}\right\}$	234·9	...	...	...	76·2	7	77	3·051	3·082
Subsulphate of zinc	$\left\{\begin{matrix}ZnO, SO_3, 3ZnO \\ +4HO\end{matrix}\right\}$	237·3	...	...	...	76·0	7	77	3·082	3·122
Protosulphate of mercury...	Hg_2O, SO_3	251·0	...	...	...	33·2	3	33	7·606	7·560
Persulphate of mercury.....	HgO, SO_3	149·6	...	...	...	23·1	2	22	6·800	6·466
Subsulphate of mercury ...	HgO, SO_3+2HgO	368·46	...	...	...	44·3	4	44	8·374	8·319
Chromate of lead	PbO, CrO_3	163·97	...	...	...	29·0	...	...	...	5·653
Subchromate of lead	PbO, CrO_3+PbO	275·7	...	...	...	44	4	44	6·266	6·266
Melanchroit	$2PbO, 2CrO_3+PbO$	439·67	...	...	...	76·5	7	77	5·710	5·750
Subnitrate of copper	$CuO, NO_5 HO+2CuO$	182·17	...	...	...	65·9	6	66	2·760	2·765
A. Subnitrate of bismuth ...	$BiO, NO_5, HO+2BiO$	300·4	...	...	...	66·0	6	66	4·551	4·551
B. Subnitrate of bismuth ...	BiO, NO_5+2BiO	291·4	...	...	...	55·4	5	55	5·298	5·260
Subpernitrate of mercury ...	$\left\{\begin{matrix}HgO, NO_5, HO \\ +2HgO\end{matrix}\right\}$	391·49	...	...	...	65·6	6	66	5·932	5·967
A. Ammonia-sulphate of copper	$CuO, SO_3, HO+2NH_3$	123·0	54	6	54	68·7	...	...	...	1·790
B. Ammonia-sulphate of copper	CuO, SO_3+NH_3	97·08	...	...	...	39·2	...	...	...	2·476
Hydrate of ammonia-sulphate of copper	$\left\{\begin{matrix}CuO, SO_3+NH_3 \\ +3HO\end{matrix}\right\}$	124·07	...	...	...	63·6	...	...	...	1·950
Ammonia-sulphate of zinc...	ZnO, SO_3, NH_3	97·8	...	...	...	39·5	...	...	...	2·479
Ammonia-turpeth	$\left\{\begin{matrix}HgO, SO_3+Hg \\ Ad+2HgO\end{matrix}\right\}$	486·0	...	...	...	66·4	6	66	7·363	7·319
Ammonia-sulphate of silver.	AgO, SO_3+2NH_3	190·86	...	...	...	65·4	6	66	2·890	2·918
Ammonia-chromate of silver	AgO, CrO_3+2NH_3	202·8	...	...	...	66·2	6	66	3·073	3·063
Ammonia-nitrate of copper .	CuO, NO_5+2NH_3	128·4	64	7	63	68·5	...	...	...	1·874
Ammonia-nitrate of mercury	$\left\{\begin{matrix}HgO, NO_5 \\ +2HgO+NH_3\end{matrix}\right\}$	399·7	...	...	...	67·0	...	...	...	5·970
Chloride of copper.....	Cu Cl	67·18	...	...	...	22	2	22	3·054	3·054
Ammonia-chloride of copper	$Cu Cl+2NH_3+HO$	110·3	63·6	7	63	66	6	66	1·671	1·671
B. Ammonia-chloride of copper	$Cu Cl+NH_3$	84·11	...	...	...	38·4	...	...	...	2·194
Subchloride of copper	$Cu_2 Cl$	98·89	...	...	...	29·2	...	...	...	3·376
Subchloride of mercury.....	$Hg_2 Cl$	238·33	...	...	...	33·2	3	33	7·221	7·178
Subchloride and amide of mercury	$Hg_2 Cl+Hg_2 Ad$	458·1	...	...	...	66·8	6	66	6·941	6·858
Chloride and amide of mercury	$Hg Cl+Hg Ad$	254·5	...	...	...	44·6	4	44	5·784	5·700
Basic chloride and amide of mercury	$\left\{\begin{matrix}Hg Cl+Hg Ad \\ +2HgO\end{matrix}\right\}$	473·3	...	...	...	65·9	6	66	7·171	7·176

The important researches of Graham have shown that water plays a most important part in the constitution of salts; and that salts with an excess of base may be viewed as hydrates, in which oxide of hydrogen becomes replaced by a metallic oxide. The previous experiments will be found to give this theory the fullest confirmation. Sulphate of zinc crystallizes with seven atoms of water and affects a volume of 74·6; and sulphate of copper assumes the same state of hydration, when crystallized with the latter salt, although *per se* it assumes only five atoms. Placing together the subsulphates and hydrated sulphates of these metals, we perceive not only a close similarity in their formulæ but also in their volumes, as ascertained by experiment.

		Difference.
$ZnO, SO_3, 3HO, 4HO$, vol.	74·6	1·4
$ZnO, SO_3, 3ZnO, 4HO$, ..	76·0	
$CuO, SO_3, 3HO, 4HO$, vol.	74·6	1·6
$CuO, SO_3, 3CuO, 4HO$, ..	76·2	

The difference between the two states of the sulphates is probably greater as stated than it actually is. We have already shown that the magnesian sulphates with seven atoms of water do not possess a volume of 77·0, because two of the atoms possess a volume of 9·8 instead of 11·0; and perhaps a similar circumstance tends to reduce the volume of the subsulphates. Similar instances of replacement of water by a metallic oxide are seen in other parts of the table. We have already shown that nitrates of copper and bismuth possess a volume of 58·8 or 9·8 × 6. We have also seen instances in which 9·8, the volume of ice, in feeble compounds, became changed into the volume 11 when the salt entered into combination. In this point of view, the subsalts $MO, NO_5 + HO + 2MO$ become assimilated to the hydrated nitrates $MO, NO_5 + HO + 2HO$, the number of volumes in both cases being the same, the only difference being, that, in the former case, the salts are multiples of 11, and in the latter of 9·8, or the volume of ice. The hydrated type affects six volumes, and so do the subnitrates, as will be seen by the following table.

$CuO, NO_5, HO + 2CuO$, volume	65·9 or	11 × 6
$BiO, NO_5, HO + 2BiO$, ...	66·0 ...	11 × 6
$HgO, NO_5, HO + 2HgO$ ...	65·6 ...	11 × 6

We have further evidence of the equivalency of water to the metallic oxide in anhydrous nitrate of bismuth, which has a volume of 55·0 or 66 − 11; the formula for the salt being $BiO, NO_5 + 2BiO$. The conversion of the volume 9·8 into 11

is by no means uncommon, and is again seen in the subchromates of lead. Chromate of lead has a volume sensibly the multiple of 9·8.

	By experiment.		By calculation.
Chromate of lead	29·0 ... 5·653	...	9·8 × 3 = 29·4 ... 5·577

Boullay gives the specific gravity of oxide of lead as 9·5, which indicates the volume 11·7, a number not far from 11, which we take as the unit volume. Subchromate of lead consists of one equivalent of the neutral chromate united to one of oxide of lead, but the three volumes of ice in the former have changed in the subsalt to 11 × 3, and the same is the case in the mineral melanchroit, which contains two equivalents of chromate of lead united to one of oxide of lead.

Subchromate of lead, $PbO, CrO_3 + PbO = 44$ or 11×4
Melanchroit, $2\,(PbO, CrO_3) + PbO = 76{\cdot}5$ or 11×7

In these salts we clearly see that oxide of lead takes up the volume and plays the part of an atom of water, although we are ignorant of their hydrated types. The same function of an oxide is seen in turpeth mineral, in which the $2HgO$, attached to HgO, SO_3, assumes the volume of two atoms of water, $22 + 22 = 44$. There can be little doubt from the previous examples of the equivalency of CuO, ZnO, BiO, HgO, and PbO, not only to each other but also to water; and this will be still more strongly seen by placing the volumes of these and other anhydrous magnesian sulphates along with the volume of sulphate of water itself, as deduced from bisulphate of potash.

Sulphate of	Water, vol. by experiment		22·0
...	Zinc	...	21·8
...	Copper	...	22·0
...	Iron	...	24·0
...	Cobalt	...	22·0
...	Mercury	...	23·1

The only cases in which there is an appreciable difference from sulphate of water are those of sulphates of iron and mercury, neither of which salts can be obtained without difficulty perfectly pure in an anhydrous state.

But if the equivalency of the magnesian metals to each other and to hydrogen be left in any doubt by the preceding table, this doubt would be entirely removed by a consideration of the magnesian chlorides. The strongest muriatic acid obtained has, according to Thomson, a specific gravity of 1·203, and contains 40·66 per cent. of dry muriatic acid; which is equal to 5·91, obviously six atoms of water to one of muriatic

acid, as pointed out by Kane. The atomic weight of this compound, divided by its specific gravity, is $\frac{90{\cdot}47}{1{\cdot}203} = 75{\cdot}2$, which is not far from 72·0 or 9 × 8, considering that the result remains uncorrected for expansion; this gives a volume of 18·0 or 9 × 2 for muriatic acid. The acid which possesses a constant boiling-point and distils over unchanged has a specific gravity of 1·094, and contains 19·19 per cent. of absolute acid, according to Davy, and 20·44 per cent. according to Thomson. The mean of their results indicates the acid to contain 16·4, or nearly 16 atoms of water. Now $\frac{180{\cdot}47}{1{\cdot}094}$ = 165, which is not far from 162, the volume of 9 × 18, making for the volume of muriatic acid in strong solutions 18·0 or 9 × 2, a result the same as that obtained by the last calculation. These results, and that given in a previous section, along with the fact that hydrochloric acid gas has twice the volume of steam, leave no doubt that muriatic acid affects two volumes; and converting the liquid into the solid volume, we have a volume of 22·0 or 11 × 2 as the atomic volume of solid muriatic acid. By contrasting this volume with the experimental results on the magnesian chlorides, we find a very great similarity.

Chloride of	Hydrogen, volume	22·0 or	11 × 2
...	Cobalt ...	22·2	...
...	Magnesium ...	22·1	...
...	Calcium ...	22·4	...
...	Copper ...	22·0	...
...	Mercury ...	22·0	...

In dilute solutions muriatic acid affects only one volume, and this has been shown to be also the case with chlorides of copper and cobalt. Whether nitrate of water and nitrate of a magnesian oxide possess the same volume it is difficult to decide. Nitrate of water in the acid of specific gravity 1·42 seems to affect four volumes, and this acid, $HO, NO_5, +3HO$ is constituted on the same type as $CuO, NO_5 + 3HO$; yet $\frac{90{\cdot}2}{1{\cdot}42} = \frac{63}{9} = 7$, which gives four volumes for HO, NO_5, while nitrate of copper certainly does not possess more than three volumes. Nitrate of water calculated on weak acids has three volumes; but there being no good fixed point upon which to make the calculation, we must leave at present this point undetermined.

An important question now arises as to the truth of the supposition that two atoms of a magnesian metal are equal to

one of the family of which potassium stands as the type. In calomel and chloride of ammonium we have a direct case in point, and the similarity of volumes is very striking.

		Diff.
Chloride of ammonium, NH_4Cl . . .	34·0	0·8
Calomel, Hg_2Cl	33·2	

In this case we have taken chloride of ammonium, because KCl assumes the volume of four atoms of ice.

Subchloride of copper, like NH_4Cl, possesses three volumes, according to Karsten's experiments and our own, but these three volumes are multiples of 9·8, and not of 11·0.

	By experiment.		By calculation.	
Subchloride of copper, vol.	29·2	3·376	9·8 × 3 = 29·4	3·363

Another illustration is furnished in sulphate of protoxide of mercury and sulphate of potash.

		Diff.
Protosulphate of mercury, vol.	33·20	0·15
Sulphate of potash	33·05	

These are instances in which two atoms of a magnesian metal are at once shown to be equivalent to one of a metal of the potash family; but it does not thereby preclude the possibility of two atoms of a magnesian *oxide* being equivalent to one atom of potash. For example, a magnesian sulphate, MgO, SO_3, affects a volume 22, or 11 × 2, while the same salt united to an atom of constitutional water has the volume 33, or MgO, SO_3HO becomes equal to KO, SO_3, which also possesses a volume of 33. The most striking case, however, is seen when crystallized subnitrate of lead is compared with nitrate of potash.

Nitrate of potash, KO, NO_5, vol.	49·0
Subnitrate of lead, $PbO, NO_5 + PbO$, vol. .	49·0

The fact that two atoms of a magnesian oxide are equivalent to one of potash, appears to find its explanation in the circumstance that we uniformly find the salt of potash assuming one volume greater than the corresponding salt of magnesia. Hence, as the volume of the oxides corresponding to the latter body is equal to unity, the equivalency of two of their atoms to one of potash becomes a matter of necessity.

To sum up these remarks, we conceive (1.) that Graham has taken the correct view in supposing subsalts to represent hydrated salts, in which water has been replaced by a metallic oxide; and (2.) that the volume of two atoms of a metal of the magnesian family, in which we include hydrogen, is equal in volume to one of the potassium group; or two atoms

of the former oxide, when combined, to one of the latter. We are now in a condition to consider the salts of ammonia.

It is quite unnecessary to remind chemists that there are two rival theories regarding the constitution of ammoniacal salts. One of them, proposed by the profound Berzelius, is that the salts of ammonia contain a hypothetical radical termed ammonium, consisting of one equivalent of nitrogen and four equivalents of hydrogen. Sulphate of ammonia is to be viewed as sulphate of oxide of ammonium, the latter hypothetical body being equivalent to potash; and hence the isomorphism between the salts of potash and ammonia. The other view of the constitution of ammonia is that proposed by Kane, and so elaborately supported by him in his paper on subsalts and ammoniacal compounds*. Dr. Kane supposes that an ammoniacal salt is formed on the type of a magnesian salt, carrying along with it constitutional water.

Sulphate of copper . . .	CuO, HO, SO_3
Sulphate of ammonia . .	HO, NH_2H, SO_3

On this view, amide of hydrogen is equivalent to, and plays the part of an atom of water. If this be the case, amidogene must be analogous to oxygen, and ammonia and a magnesian oxide must possess the same atomic volume. At present all this is purely hypothetical, and must be subjected to the test of experiment before we can admit it as a safe foundation on which to rear a theory. The means of deciding this question seemed to present itself in an examination of the amides of mercury, and of the crystallized salts of copper and zinc, in which the ammonia is present *quasi* ammonia; and such compounds have been described in the beautiful researches of Kane on this subject. Wöhler's white precipitate, $HgCl + NH_3$ seems to be constituted in the most simple manner, and possesses a volume of 33·0, which, deducting the volume 22·0 for HgCl, leaves 11·0, or unity, as the volume of NH_3. But again, white precipitate, $HgCl + HgNH_2$, affects a volume of 44·6 by experiment, which, deducting 22·0 for HgCl, leaves $HgNH_2$ also equal to 22·0, and yet the latter compound should correspond in volume to NH_2H. The heavy yellow powder obtained by boiling white precipitate with water has a volume of 66·0, and is constituted according to the formula $(HgCl + HgAd) + 2HgO$; so that deducting 44·0, the ascertained volume of the double amide and chloride, 22 or 11×2 remains for *two* atoms of HgO, giving the same result as in the former subsalts, viz. the equivalency of HgO to HO, but not to $HgNH_2$; and another proof of this is afforded in the

* Transactions of the Royal Irish Academy, vol. xix. part 1.

reduction of the volume of ammonia turpeth. From this circumstance, the view would appear probable that amide and chloride of mercury are equivalent, and hence would follow the equivalency of chlorine to amidogene. This receives further support from the volume of the double subamide and subchloride of mercury, $Hg_2Cl + Hg_2Ad$, which has a volume of 66·8, according to experiment. Calomel itself possesses the volume 33·2, which, deducted from that of the salt just described, gives 33·6 as the volume of Hg_2Ad, showing the complete equivalency of the latter to the subchloride.

It has been shown that chloride of mercury and chloride of hydrogen are equivalent, and it now remains to be shown by direct proof that amide of hydrogen (ammonia) is embraced in the same category. Ammonia-chloride of copper, $CuCl + NH_3$, was found with a volume of 39·2 or $9·8 \times 4$; chloride of copper itself affects two volumes, which leaves for Ad, H, as deduced from this salt, also two volumes. But the ammonia in $CuCl + 2NH_3 + HO$, if we were to suppose the salts constituted in a manner so simple as expressed by their empirical formulæ, would only have a volume of 33·0 for two atoms, or $1\frac{1}{2}$ volume for each.

In proceeding further, it will be seen that we involve ourselves in inextricable difficulties, if we insist upon the equivalency of NH_2H to HO; or suppose the ammoniacal salts, such as those described, to be constituted on the type of the hydrated salts. Thus, ammonia-sulphate of copper, $CuO, SO_3 + 2NH_3 + HO$, has a volume of 68·6 or $9·8 \times 7$ in its solid state, and of 54 or 9×6 when in solution. Deducting 19·6 for CuO, SO_3, and 9·8 for HO, there is again left 39·2, or $9·8 \times 4$ for *two* atoms of ammonia. The simple salt, $CuO, SO_3 + HN_3$, has a volume of 39·2, which leaves 19·6, or $9·8 \times 2$ for one atom of ammonia; but the same salt, when combined with three atoms of water, yields the volume 63·6, which would lead us to suppose that one atom of water is equal to one atom of ammonia. We also find ammonia with the volume 11, or unity, when calculated from the observed volume of hydrated sulphate of ammonia. But in the ammonia-chromate of silver, $AgO, CrO_3 + 2NH_3$, and in its corresponding sulphate, we find on deducting 33·0, or 11×3 for the salts themselves, the residual 33·0 for *two* atoms of ammonia. Again, however, we become perplexed by finding that the ammonia in ammonia-pernitrate of mercury possesses the volume of an atom of water. Thus, then, by considering the volumes of the ammoniacal salts as containing their ammonia *quasi* ammonia, and as constituted on the type of the hydrated salts, we obtain the contradictory and absurd result, that ammonia, though

often taking a volume equal to unity, sometimes possesses a volume of $1\frac{1}{2}$, and occasionally two volumes. It is pretty certain, from these contradictory results, that the salts are not constituted on the hydrated type.

Graham has thrown out the ingenious idea*, that the salts now referred to may actually contain an ammonium in which the fourth equivalent of hydrogen is replaced by an equivalent of a magnesian metal. Thus $CuO, SO_3 + NH_3$ is constituted, according to Graham, NH_3Cu, O, SO_3, on the type of sulphate of ammonia, NH_3H, O, SO_3. There is nothing whatever opposed to this view in Kane's researches, as he himself admits, the only difference being that he considers the said salts to contain oxide of copper and water united to amide of hydrogen, instead of to *cuprammonium* and oxide of ammonium, according to the views of Berzelius and Graham. While, therefore, Kane admits that amide of hydrogen is very closely allied to chloride of hydrogen, he claims for the former body an equally close alliance to water, by asserting that it is equivalent to a magnesian oxide, although it is difficult to conceive why chloride of hydrogen has not a right to a similar claim. Amide and chloride of mercury have undoubtedly the same volume, viz. 22·0, and chloride of hydrogen also enjoys the same number; but water does not in any case do so. On this point alone, then, are we at issue with Kane, for there are many proofs that there is extreme probability in the view propounded by him of the presence of NH_2H and HO in ammoniacal salts. On the former view alone do we contest the accuracy of the opinion, leaving for future consideration and research, to which we are now devoting ourselves, a more defined notion of the reason why NH_2H and HO are equivalent in many instances, *not* in *all*, to potash. We have already stated the incongruous results which would flow from the conception that ammonia was simply attached to the salts examined. It is true that Kane gives to some of them a constitution more intimate, and when he does so his theory accords with our results. But his conception of the equivalency of NH_2H to HO has led him in other instances to attach the ammonia to the salt in place of water, and it is from these cases that we dissent. If he merely means that NH_2H can replace HO in a compound, as KO, SO_3 does in a magnesian sulphate, then we cease to differ, because the resulting compounds do not remain in strict parallelism; the only point we argue against being that HO and NH_2H are equivalent. Thus we have, supposing all of them to affect the primitive volume 9·8,—

* Graham's Elements of Chemistry, p. 416.

$$HgO, NO_5 + HgO + 2HO = 6 \text{ vol.}$$
$$HgO, NO_5 + HO + 2HgO = 6 \ldots$$
$$HgO, NO_5 + NH_3 + 2HgO = 7 \ldots$$

The first two members of the series have the same number of volumes, because HgO and HO are equivalent, and the last salt should also affect the same, if $NH_2H = HO$. But if we consider the last salt as equal to nitrate of ammonia, in which HgO replaces HO, then it becomes intelligible.

$$NH_2H, HO, NO_5 \text{ affects } 5 + 2 \text{ of } HO = 7$$
$$NH_2H, HgO, NO_5 \ldots \quad 5 + 2 \text{ of } HgO = 7$$

On the same principle we would arrange the other ammoniacal compounds. Thus $CuO, SO_3 + NH_3$ obviously ought to be arranged NH_2H, CuO, SO_3, corresponding to NH_2H, HO, SO_3, anhydrous sulphate of ammonia, and both affect, as they should do on this formula, four volumes. We observed a very decided peculiarity in sulphate of ammonia; for while in its hydrated condition the NH_4O, SO_3 could only be equal to three volumes, in its anhydrous state, or when in combination with salts, it assumed four volumes. The latter peculiarity attends the *alpha* ammonia-sulphate of copper, and is shared also by ammonia-sulphate of zinc, while the hydrate assimilates itself to $NH_4O, SO_3 + HO$.

$$NH_2H, HO, SO_3 = 39{\cdot}2$$
$$NH_2H, CuO, SO_3 = 39{\cdot}2$$
$$NH_2H, ZnO, SO_3 = 39{\cdot}2$$
$$(NH_2H, CuO, SO_3 = 39{\cdot}2) + (HO = 9{\cdot}8) + (NH_3 = 19{\cdot}6) = 68{\cdot}6$$
$$NH_2H, HO, SO_3 + HO = 44$$
$$(NH_2H, CuO, SO_3 + HO = 44) + (2HO = 19{\cdot}6) = 63{\cdot}6$$

In ammonia-nitrate of copper we have an instance in which the ammonia may be present either as nitrate of ammonia or as ammonia; for if we suppose the volume 68·5, which obviously indicates $9{\cdot}8 \times 7 = 68{\cdot}6$, to be made up of $CuO, NO_5 + 2NH_3$, we must assume that two atoms of ammonia are equal to four atoms of ice, for we already have seen that CuO, NO_5 affects three volumes. On the supposition that the compound contains a substance equivalent to nitrate of ammonia, the volumes are equally intelligible.

$$NH_2H, HO, NO_5 = 49{\cdot}0$$
$$NH_2H, CuO, NO_5 = 49{\cdot}0 + NH_2H = 19{\cdot}6 = 68{\cdot}6$$

Perhaps, however, the clearest instances are seen in the ammoniacal chromate and sulphate of silver. AgO, CrO_3 and AgO, SO_3 affect a volume of $9{\cdot}8 \times 3$, and supposing a transformation into multiples of 11, of which we have seen frequent instances, $2NH_3 = 33{\cdot}0$, or $NH_3 = 16{\cdot}5$, or $1\frac{1}{2}$ times the

number which we assume as unity. But on the supposition that AgO takes the place of HO, the difficulty ceases.

NH_2H, HO, SO_3 = 44
NH_2H, AgO, SO_3 = 44 + NH_2H = 66
NH_2H, AgO, CrO_3 = 44 + NH_2H = 66

Perhaps the most anomalous salt in the whole series examined is chloride of ammonium, which actually decreases one volume in becoming solid, 9 × 4 in solution being 11 × 3 in the state of a salt. Chloride of potassium refuses to share this anomaly, and we accordingly find it 9·8 × 4, and NH_4Cl associates itself to KCl in the double salts. Four volumes for NH_4Cl is undoubtedly what we should expect from its composition, and from that number being affected in solution and in its double salts. We also see the three volumes entering into *alpha* ammonia-chloride of copper, although the beta, according to our results, seems singularly enough to affect the proper four volumes.

NH_2H, HCl = 33
NH_2Cu, HCl = 33 + NH_2H = 22 + HO = 11 = 66
NH_2Cu, HCl = 38·4 or 9·8 × 4 = 39·2

The double amides and chlorides, as we have already shown, affect the same number of volumes as NH_4Cl when in solution, and might be placed on the same type as NH_2Hg, HCl. Without denying that NH_2H and HO may be so intimately associated in the ammoniacal salts as to form the hypothetical body oxide of ammonium, we would call attention to the facts, which show that the resulting volumes of the ammoniacal salts are made up of the volumes of the hydrated acid and amide of hydrogen. It by no means militates against that view, that in hydrated sulphate of ammonia we have one volume in solution less, and also in the state of a solid, than should result from the combination of these two. CuCl has undoubtedly *per se* two volumes, just as HCl has in a concentrated state, or as NH_2H has in combination. But the CuCl in CuCl + 2HO possesses only one volume, the other having disappeared in the water; and HCl itself has only one volume in dilute solutions. The disappearance of one volume in combination with water is by no means so surprising as the disappearance of the volumes of 23 atoms of the constituents of alum in the water in which it is dissolved, especially when we find the salt under consideration, sulphate of ammonia, vindicating its proper volume when in combination. The oxalate of ammonia has its *proper* volume, just as has anhydrous sulphate of ammonia; the only exception is the decidedly anomalous salt—chloride of ammonium, although this also ceases

to be anomalous in the double chlorides. By placing together the volumes of the hydrated acids and those of the ammoniacal salts, it will be seen that the latter are made up of the volumes of the hydrated acid united to amide of hydrogen affecting two volumes, like HCl.

Sulphate of ammonia $= HO, SO_3 = 2 + NH_2H = 2 = 4$
Nitrate of ammonia $= HO, NO_5 = 3 + NH_2H = 2 = 5$
Oxalate of ammonia $= HO, C_2O_3 = 2 + NH_2H = 2 = 4$

All the ammoniacal salts which we have described in this section may be arranged in a similar way with a like result.

We do not profess to have resolved the cause of the equivalency $HO + NH_3$ to KO; nor do we insist that they do not enter into more intimate union to form NH_4O. It must not be left out of consideration, however, that in almost every instance the ammoniacal salt affects one volume in solution more than the corresponding salt of potash, and that the number of volumes of the latter becomes augmented by one in passing from the liquid to the solid state, while the number of volumes of the ammoniacal salt remains unchanged. It requires a more minute knowledge of the constitution of salts than we now possess to decide the question at issue.

Conclusion.

Although we have examined many other salts than those described in the previous pages, with results quite confirmatory of our views, we do not feel warranted in extending our memoir, already much too long. We therefore conclude by summing up, in the form of propositions, the laws which we consider regulate the volumes of salts. At the same time we do so with strict reference to the salts which we have described, deprecating their hasty generalization, being ourselves quite satisfied that there are peculiarities in other cases, which must be subjected to close examination. This being only the first of several memoirs on the same subject which we intend to lay before the Society, we do not present this investigation as being in itself complete.

Prop. I.—*Compounds dissolved in water increase its volume for every equivalent either by* 9, *or by multiples of* 9.

This, in other words, signifies that the volumes of salts in solution are either equal to each other, or are multiples of each other; for 9, being the volume of nine grains, or an equivalent of water, is merely assumed as the standard of comparison.

a. Certain salts, such as the magnesian sulphates, the

alums, &c., dissolve in water without increasing its bulk more than is due to the liquefaction of the water which they themselves contain; the anhydrous salt taking up no space in solution.

b. Anhydrous salts, or salts containing a small proportion of water, affect a certain number of volumes in solution, which pass along with them unchanged into their union with other salts.

c. The volume occupied by double salts when dissolved is the sum of volumes occupied by their constituents when separate, with the exception of certain cases described in the previous sections.

Prop. II.—*The volume occupied by a salt in the solid state has a certain relation to the volume of the same salt when in solution; and has also a fixed relation to the volume occupied by any other salt.*

a. The volume of an equivalent of any salt is either 11, or a multiple of 11, or of a number very nearly approaching the number 11.

b. Or the volume of a salt is 9·8, or a multiple of 9·8, or, in other words, of the volume occupied by an equivalent of solid water (ice).

c. Or the volume of a salt is made up of a certain multiple of the number 11, added to a certain multiple of the number 9·8.

On each of these heads we would offer a few remarks.

With two assumptions we have been enabled to connect with each other the volumes occupied by all the salts examined by us in the previous sections. These assumptions are, that the divisor for the volumes of salts is either 11, or a number very nearly approaching to it, or that the divisor is 9·8, the volume of ice itself.

We have been guarded in stating positively that the first divisor is absolutely 11, because we do not in the present memoir enter into the connection between this number and the volume of ice, 9·8. To show, however, that our experiments agree with those of recent accurate experimenters, and that the number 11, which we have at present to announce empirically, cannot be wide from the truth, we append the theoretical and experimental results upon the alums, which we stated to possess twenty-five volumes, in which therefore any considerable error in the number 11 would be multiplied by 25, and plainly show itself in the results. Notwithstanding this severe test, it will be seen that the theoretical and experimental numbers are actually within the errors of the balance.

	Theoretical. sp. gr.	By Kopp's* experiments.	By our experiments.	Mean of experiments.
Potash alum .	1·727	... 1·724	... 1·726	... 1·725
Chrome alum	1·833	... 1·848	... 1·826	... 1·837

The number 11 must then be very near the truth, if it be not absolutely the truth. We now append an equally severe test for our view that the volumes of many salts are multiples of 9·8, the number representing the volume of ice. If there be an error in this number, it must become very notable in the phosphates and arseniates, when multiplied by 24, or in carbonate of soda when multiplied by 10. Perhaps sugar itself will form as severe a test as could be desired, for we proceed on the extraordinary fact that the 12 atoms of carbon in sugar have ceased to occupy space, and that the bulk of an atom of sugar is just the bulk of H_{11} O_{11}, or its 11 atoms of hydrogen and oxygen, *quasi* water, frozen into ice.

	Theoretical sp. gr.	Sp. gr. according to our experiments.	Other authorities.
Carbonate of soda .	1·463	1·454	1·423 Haidinger.
Phosphate of soda .	1·527	1·525	1·514 Tünnerman.
Subphosphate of soda	1·622	1·622	none
Arseniate of soda .	1·713	1·736	1·759 Thomson.
Subarseniate of soda	1·808	1·804	none
Cane-sugar . . .	1·591	1·596	1·600 Schübler & Renz.

Thus even in salts so difficult to obtain in a proper degree of hydration free from mechanical water, as those given in the above table, the difference between the theoretical and experimental numbers is not greater than might have been expected.

We give one other class of salts to illustrate position *c* in Prop. II., there being in these salts a certain number of volumes represented by 11, and a certain number by 9·8, CuO, SO_3 representing the number of volumes with the divisor 11.

	Theoretical sp. gr.	Sp. gr. by our experiments.	Sp. gr. by other authorities.
Sulphate of copper .	2·270	2·254	2·274 Kopp.
... zinc . .	1·926	1·931	1·912 Hassenfratz.
... iron . .	1·854	1·857	1·840 *Idem.*
... magnesia	1·660	1·660	1·660 *Idem.*
... nickel .	2·033	...	2·037 Kopp.

We have selected these three classes of salts as being the most severe tests which we could apply to our theory, and any chemist who has had experience in this subject will at once admit that the theoretical and experimental numbers are

* *Annalen der Pharmacie*, Bd. xxxvi. S. 10.

as near each other as the estimation of specific gravities by any two different experimenters. We do not rest the claims of our theories on our own experiments, but are willing to admit the accuracy of other experimenters, especially of Karsten, Hassenfratz, Kopp, and others who have preceded us on this subject*; while at the same time we believe that our methods of taking specific gravities have enabled us to introduce more uniformity into the results. The simplicity of the methods themselves is due to Bishop Watson, who was the first to take specific gravities by the increase in the stem of an instrument; and to Holker the suggestion is due of using a saturated solution instead of the water employed by Watson.

We conceive that the primitive volume 9·8 is transformable into the primitive volume 11, and *vice versâ*, and for this reason we sometimes see sulphate of ammonia $9{\cdot}8 \times 4$, at other times, in combination as in bisulphate of ammonia or the anhydrous double sulphates, it is 11×4; and numerous other instances of transformation are presented in the previous sections.

The liquid volume being to the solid volume either as 9 : 11 or as 9 : 9·8, these numbers, used as the divisor for the liquid and solid volumes respectively, usually yield the same quotient. Thus the liquid volume of sulphate of copper is 45, its solid volume is 55. $\frac{45}{9} = 5$, and $\frac{55}{11} = 5$; so that we say the salt affects the same number of volumes in the liquid and in the solid state. In the same manner subphosphate of soda has a volume of 216 in solution and of 235 in the state of salt. Now $\frac{216}{9} = 24$ and $\frac{235}{9{\cdot}8} = 24$, so that the number of volumes affected in solution and in the solid state are exactly the same. This is a general rule and a powerful argument of the accuracy of our position. The rule has exceptions in salts of potash, in which the volumes are increased by one volume on becoming solid; thus $KO, SO_3 = \frac{18}{9} = 2$ in solution, and $\frac{33}{11} = 3$ in the solid state. This is

* The only decided difference which we found from other experimenters is in the case of hydrated salts. Thus our determination of the volumes of the double magnesian sulphates and sulphate of potash (Table VI.) differs from Kopp's experiments as 99 : 103. These salts contain from 3 to 4 per cent. of mechanical water, as Graham long ago pointed out (Trans. R. S. E. vol. xiii. p. 12), and the neglect of this in Kopp's experiments has probably caused the difference. We take this opportunity of stating that when more than one specific gravity is given by us, the salts have been prepared at different times; in many instances this is not the case, but in much the largest proportion it is so.

not an accidental variation, but an actual augmentation of one volume, as is proved by the potash alums, in which KO, SO_3 has ceased to occupy space in solution, but on the crystallization of the alum the volume becomes increased by one, obviously owing to this peculiarity of KO, SO_3; thus alum in solution $\frac{216}{9} = 24$, becomes $\frac{275}{11} = 25$ in the state of a salt.

This peculiarity is very striking, especially in the case KO, CO_2, which with a volume of $\frac{33}{11} = 3$ as a solid, becomes $\frac{9}{9} = 1$ as a liquid. Let us endeavour to conceive the extraordinary amount of power exerted in this case; the water in the volumenometer, on dissolving an equivalent of KO, CO_2, descends from 33 to 9, so that a bulk of solid matter = 24 grains of water disappears within it. If we would compare the force to that which would be required to compress the water into this diminished bulk, we must deal in numbers of a magnitude truly immense. We have always been accustomed to view as an exception the expansion of water on becoming solid, but now we see with Longchamp, that the rule is universal; the salt (muriate of ammonia excepted?) takes up more space as a solid than it does in its liquid state in solution.

We have stated that we desire not to be held responsible for any rash generalization of these laws, which we do not extend at present beyond the salts examined by us. Let us consider the volumes of the ammonia alums, as an example of the danger of applying either of the laws without a proper comprehension of them. These volumes are certainly above 275, the volumes of the potash alums, and are between 279 and 280, according to our experiments and those of Kopp. Now let us suppose that the four volumes of NH_4O, SO_3 are represented in the alums, and that only Al_2O_3, $3SO_3$ has ceased to occupy space, as it in fact does when hydrated, then an ammonia alum Al_2O_3, $3SO_3 + NH_4O$, $SO_3 + 24HO$ may be viewed as $9{\cdot}8 \times (24 + 4) = 279{\cdot}4$, and the specific gravities would countenance this idea.

	Sp. gr. by Theory.	Sp. gr. by our experiments.	Sp. gr. by Kopp's experiment.
Ammonia alum . .	1·626	1·625	1·626
Ammonia iron alum	1·721	1·718	1·712

These results certainly approach the theoretical number very closely; and the theory may represent the truth. But at the same time it is difficult to believe that the ammonia alum is constituted on a different type from the potash alum. We might suppose that the only variation between them is the

difference between the volumes of KO, SO_3 and NH_4O, SO_3, or the difference between 11×3 and $9{\cdot}8 \times 4$. This difference, 6·2, added to the volume of potash alum $275 + 6{\cdot}2 = 281{\cdot}2$, which is not very wide from the experimental results, and would give the specific gravity by theory for ammonia alum 1·616, and for ammonia iron alum 1·711. These are points which require further inquiry.

We do not refer here to the minor views embraced in the preceding investigation, being anxious principally for inquiry and confirmation into the three main theories propounded. With one assumption for the volume in solution, and with two assumptions for the volumes of solids, we have been enabled to explain, as we trust, the specific gravities detailed in the previous sections. We might perhaps with propriety indulge in speculation, and apply these laws in explanation of isomorphism and dimorphism, but we prefer the safer course of trusting to experimental investigation, part of which we shall in a short time lay before the Society in an inquiry upon the expansion of solutions, and on some other points connected with this important subject.

ERRATA.

Page 12, *for* $C_8 N_2 H_4 O_8 = C_8 N_2 H_3 O_7 + HO$ *read* $C_8 N_2 H_5 O_9 = C_8 N_2 H_4 O_8 + HO$.
—— 228, *for* chlorisatin and bichlorisatin *read* chlorisatine and bichlorisatine.
—— 228, 229, 234, 249, 251, 252, 253, 254, *for* anilene *read* aniline.
—— 269, *for* phenyl *read* phenyle.

INDEX.

ACIDS:—meconic, 1, 114; komenic, 1, 7, 117; pyromeconic, 2; pyromucic, 5; pyrokomenic and parakomenic, 6; uric, 9; dialuric, 11; acid thionurate of ammonia, 13; alloxano-sulphurous, *ib.*; alloxanic, 14; ferric, 25; catechuic, 45; neutralization of various, by hydrate of potash, 51; of hydrate of potash by nitric, sulphuric, and hydrochloric, 52, 58; of acetic, oxalic, arsenic and phosphoric, by hydrate of potash, 65, 68; action of, upon spathic carbonate of iron, 106; on some salts of meconic and komenic, 113; iron salt from æthereal solution of meconic, 116; on separating lime and magnesia when they exist in combination with phosphoric, 140; opianic, 172; hemipinic, 172; on sulphuric, phosphoric and carbonic, in vegetable ashes, 182, 189, 190; acids in Bonnington water, 207; in bones from guano, 225; kinic, 226; action of nitric, on chloraniline and on styrole, 283, 339; benzoic, 342; nitrobenzoic, 343; action of chromic and sulphuric, on styrole, and of nitric, on metastyrole, 344, 345, 351; phosphoric, in the deep-well water of the London basin, 392.

Actino-chemistry, contributions to, 311.

Æthogen, 15.

Alaria esculenta, mannite contained in, 138.

Alkalies in vegetable ash, 188, 190.

Alkaline earths in vegetable ash, 187.

Alloxanic acid, 14.

Alloxano-sulphurous acid, 13.

Alloxantine, 10.

Alloy of zinc, iron, lead and copper, on a crystallized, 393.

Alums, volumes of certain, 414.

American guano, composition of some varieties of South, 140; analysis of samples, 149, 150.

Ammonia, komenate of, 8; dialurate of, 11; acid thionurate of, 13; komenate of, 118; new mode of estimating, 140; in the Bonnington water, 215; decomposition of salts of, 244.

Analyses:—pyromeconic acid, 2; parakomenic acid, 7; komenate of peroxide of iron, 8; catechu and cutch, 47; of a silver vase found between Bow and Stratford, 48; double sulphates, 50; of recent and fossil bones, 98; spathic carbonate of iron, 105; meconic acid, 113; meconate of lead, 114; komenate of ammonia, lead, copper and silver, 118, 119, 120; hydrate of the oil of turpentine, 121; East Indian grass oil, 123; *Laminaria saccharina*, 137; South American guano, 149; concrete guano, 151; saline guano, 152; narcotine, 163; vegetable ashes abounding in silica, 190; ashes of tobacco, wheat, rye, peas, the apple-tree, 192, 193; of seed-ashes containing tribasic and bibasic phosphates, 195, 197; diseased wheat, 199; of the Bonnington water, and the soluble and earthy ingredients in the, 201, 206, 211; carbonic acid gas and ammonia, 215; of bones from the guano, 225; chloranil, 230; green glass, 248; hydrochlorate of chloraniline, 280; farm-yard manure and coal-gas, 309; brown iron ore, 322, 324, 325; hydrochlorate of toluidine, 379; of gingerade, 386; of zinc plates, 394.

Andropogon Ivaracusa, oil of the, 122.

Aniline, on the formation of, 249; action of chlorine on, 270.

Anniversary Report and Address, 109, 329.

Antimony, solubility of, 20.

Apple-tree, analysis of the ash of, 193.

Arrott (A. R.) on a class of double sulphates, containing soda and a magnesian oxide, 49.

Arseniates, volumes occupied by, 418.

Arsenic, solubility of, 20; improved

method for the detection and quantitative determination of, 129; decoloration and solution of substances by, 130; separation of the, as sulphuret of, *ib.*; purification of sulphuret of, 131; quantitative determination of the sulphuret of, *ib.*; reduction of the sulphuret of, 132.
Ash-analysis, method of quantitative, 184.
Ashes, vegetable, inorganic compounds in the normal, 182; rich in alkaline and earthy carbonates, 183, 186; in alkaline and earthy phosphates, 184, 186; in silica, 184, 190; preparation of the, 184; carbonic acid in, 190.
Ashes of tobacco, analysis of the, 192.
Atomic volume, on, 401.
Auditors' Report, 112, 333.
Balmain (W. H.) on æthogen, 15.
Baryta, action of anhydrous, and lime, on chloraniline, 284.
Benzoic acid, 342.
Bicarbonate of potash, neutralization of, with hydrate of potash, 68.
Bichloride of platinum, products of decomposition of narcotine by, 163, 168.
Bichromate of potash, neutralization of, by hydrate of potash, 64.
Binoxalate of potash, 66.
Bismuth, solubility of, 20.
Bleaching powder, action of, on the salts of copper and lead, 387.
Blyth (Dr. J.) on the composition of narcotine, and some of its products of decomposition by the action of bichloride of platinum, 163; on styrole, and some of the products of its decomposition, 334.
Bones, occurrence of fluorine in recent as well as in fossil, 97, 134; curious change in the composition of, taken from the guano, 223.
Bonnington water, analysis of the, 201.
Bromaniline, composition of, 290; properties of, 291; oxalate of, *ib.*; hydrochlorate of, 292; bichloride of platinum, 293.
Bromides, 440; volumes in solution and in the solid state of certain, 446.
Bromine, in the Bonnington water, 209; production of organic bases which contain, 266; action of, on chloraniline, 283; on styrole, 345.
Bromisatine, action of fused hydrate of potash on, 289; compounds of, 291.
Bromostyrole, 345.
Bunsen (Prof.) on the direct formation of cyanogen from the union of the nitrogen of the air with carbon, 391.
Burnard (C. F.) on a modification of the apparatus for estimating the carbonic acid in carbonated alkalies, &c., 199.
Cadmium, solubility of, 19.
Calamus aromaticus, oil of the, 122.
Cane-sugar, on the conversion of, 384; volumes occupied by, 418.
Carbonate of iron, spathic, 105.
Carbonates, vegetable ashes rich in alkaline and earthy, 183; analysis of, 186; atomic volume of, 453; volumes occupied by the alkaline, 454.
Carbonic acid in vegetable ash, 190; on the apparatus for estimating the, in carbonated alkalies, &c., 199.
Carty (John) on a new cyanide of gold, 80; on a specimen of diseased wheat, 199.
Catechu, analysis of, 47.
Catechuic acid, 45.
Cellulose and inulin, on the conversion of cane-sugar into a substance isomeric with, 384.
Cerealia, oxide of copper in, 183.
Charcoal, determination of the silica of the, in vegetable ash, 186; action of animal, 326.
Chemical combination, actinic influence on, 317.
Chemical lamp-furnace, on a, 218.
Chinolin and leucol identical, 384.
Chloranil, 227.
Chloraniline, 273; properties of, 274; compounds of, 276; sulphate of, 277; binoxalate of, 278; phosphate of, 280; hydrochlorate of, *ib.*; products of the decomposition of, 281; action of the oxygenated compounds of chlorine on, *ib.*; action of chlorine on, 283; of bromine on, *ib.*; of nitric acid on, *ib.*; of anhydrous baryta and lime on, 284; of potassium on, 285.
Chlorides, 440; volumes in solution and in the solid state of certain, 446, 447.
Chlorindatmit, on the true composition of, 306.

Chlorine, in vegetable ash, 189; in the Bonnington water, 208; decomposition of oxides and salts by, 234; production of organic bases which contain, 266; action of, on aniline, 270; of the oxygenated compounds of, on chloraniline, 281; action of, on chloraniline, 283; on styrole, 346.
Chlorisatine, action of fused hydrate of potash on, 272.
Chloro-carbon, oxalate of, 365.
Chlorodibromaniline, 288.
Chlorostyrole, 346.
Chromates, 448; volumes occupied by certain, 450.
Chromic acid, action of, on styrole, 344.
Cinnamole, 353.
Clark (Dr.) on the removal of lead, the chief poison to be apprehended in water, by an effective filter, 384.
Coal-gas, analysis of, 309.
Cobalt, solubility of, 20.
Compounds, conjugate, 360.
Cooper (John Thomas) on catechuic acid, 45.
Copper, pyromeconate of, 3; komenate of, 119; discovery of pure oxide of nickel in the scum arising from smelting of, 384; action of bleaching powder on the salts of, 387.
Cotarnin, formation of hydrochlorate of, 171.
Couch grass, supposed existence of mannite in the roots of, 139.
Crum (Walter) on the action of bleaching powder on the salts of copper and lead, 387.
Cutch, analysis of, 47.
Cyanide, of gold, 80, 82, 86; of potassium, 82, 92; of gold and potassium, 88; of silver, 92; decomposition of the double, by an electric current, 158.
Daubeny (Dr. Charles) on the occurrence of fluorine in recent as well as in fossil bones, 97.
De la Rue (W.) on the structure of electro-precipitated metals, 300; on a crystallized alloy of zinc, iron, lead and copper, 393.
Dialurate of ammonia, 11.
Dialuric acid, 11.
Dibromaniline, composition of, 294; properties of, 295.
Dibromisatine, action of fused hydrate of potash on, 294.
Dichloraniline, 285.
Dichlorisatine, action of the fused hydrate of potash on, 285.
Draconyl, 357.
Drayton's (Mr.) new method of covering glass by precipitation with a coating of metallic silver, 128.
Earths, alkaline, in vegetable ash, 187.
East Indian grass oil, on, 122
Electric current, decomposition of the double cyanides by an, 158; on the decomposition of metallic salts by an, 255.
Electro-chemical action, actinic influence on, 319.
Electro-precipitated metals, on the structure of, 300.
Fermentation, observations on, 21.
Ferric acid, on, 25.
Fluids, on the circular polarization of light by transmission through, 26.
Fluoride of iodine, preparation of, 162.
Fluorine, occurrence of, in recent as well as in fossil bones, 97; and the sources from whence it is derived, 134.
Fresenius (Dr. Remigius) on an improved method for the detection and quantitative determination of arsenic, 129; on the inorganic constituents of plants, 179.
Fucus vesiculosus, *F. serratus*, and *F. nudosus*, mannite contained in, 138, 139.
Furnace, on a chemical lamp, 218.
Furze (John N.) on fermentation, 21.
Gas, carbonic acid, amount contained in the Bonnington water, 215.
Gas-lime, composition of, 359.
Genth (M.) on the discovery of pure oxide of nickel in the scum arising from smelting of copper, 384.
Gingerade, analysis of, 386.
Glassford (Charles F. O.) on the cyanides of the metals, and their combinations with cyanide of potassium: —Part I. Cyanide of gold, 82; Part II. Cyanide of silver, 92.
Glass, on some commercial specimens of green, 247.
Gold, solubility of, 20; cyanide of, 80, 82, 86.
Graham (Thomas) on the heat disengaged in combinations, 51; on the

useful applications of the refuse-lime of gas-works, 358; on the existence of phosphoric acid in the deep-well water of the London basin, 392.
Grass oil, East Indian, 122.
Gravity, on specific, 401.
Gregory (Dr.) on the chemical history of the products of the decomposition of uric acid, 9; on a new phosphate of magnesia, 310.
Guano, composition of some varieties of South American, 140; analysis of samples of, 149, 150; of concrete, 151, 152; of saline, *ib.*; on bones taken from the, 223.
Halydris siliquosa, mannite contained in, 138.
Hemipinic acid, 172.
Hodges (Dr. J. F.) on the pharmaceutical and chemical characters of the Peruvian matico, 123.
Hofmann (A. W.) on chloranil, 227; on certain processes in which aniline is formed, 249; on the metamorphoses of indigo—production of organic bases which contain chlorine and bromine, 266; on the true composition of chlorindatmit, 306; on styrole, and some of the products of its decomposition, 334; on toluidine, a new organic base, 367; leucol and chinolin identical, 384.
Hunt (R.) on actino-chemistry, 311.
Hydrate of the oil of laurel turpentine, 121.
Indigo, metamorphoses of, 266.
Inulin, on the conversion of cane-sugar into a substance isomeric with cellulose and, 384.
Iodides, 440; volumes in solution and in the solid state of certain, 447.
Iodine, preparation of fluoride of, 162; in the Bonnington water, 208.
Iron, pyromeconate of, 4; komenate of peroxide of, 8; on the solubility of the metals in persulphate and perchloride of, 16; spathic carbonate of, 105; meconic acid and the persalts of, 114; reduction of the salts of peroxide of, by means of vegetable substances, 120; peroxide of, in vegetable ash, 187; oxide of, contained in the Bonnington water, 218.
Iron ore, on brown, 321; composition and quantitative analysis of, 322.
Iron salt from æthereal solution of meconic acid, 116.
Isatine, action of hydrate of potash in fusion on, 271.
Jones (Dr. H. Bence) on the decomposition of salts of ammonia at ordinary temperatures, 244.
Joule (J. P.) on atomic volume and specific gravity, 401.
Kinic acid, on detecting, 226.
Kolbe (Dr. H.) on conjugate compounds, 360.
Komenate of peroxide of iron, 8; of ammonia, 8, 118; of lead, *ib.*; of copper, 119; of silver, 120.
Komenic acid, products of the distillation of, 6; preparation of salts of, 113, 117.
Laminaria saccharina, and other seaweeds, occurrence of mannite in the, 136, 138.
Lead, solubility of, 19; meconate of, 113; komenate of, 118; action of bleaching powder on the salts of, 387; solubility of oxide of, in pure water, 399.
Leeson (Dr. H. B.) on the circular polarization of light by transmission through fluids, 26; on the preparation of fluoride of iodine, 162.
Leucol and chinolin identical, 384.
Light, on the circular polarization of, by transmission through fluids, 26.
Lime, process of separating the phosphate of, from magnesia, 142; on a new hydrated phosphate of, 222; action of anhydrous baryta and, on chloraniline, 284; useful application of the refuse, of gas-works, 358; composition of gas, 359.
Liquids, table of some rotating, 44, 45.
London basin, existence of phosphoric acid in the deep-well water of the, 392.
Maclagan (Dr. Douglas) on the conversion of cane-sugar into a substance isomeric with cellulose and inulin, 384.
Magnesia, on separating the phosphate of lime from, 142; on a new phosphate of, 310.
Mannite, occurrence of, in the *Laminaria saccharina* and other seaweeds, 136; supposed existence of, in *Triticum repens*, or couch grass, 139.
Manure, analyses of farm-yard, 309.
Matico, Peruvian, on the pharmaceu-

tical and chemical characters of the, 123.
Meconate of lead, 113.
Meconic acid, products of the distillation of, 1, 6; salts of, 113; and the persalts of iron, 114; iron salt from æthereal solution of, 116.
Mercury, bichloride of, and chloraniline, 281.
Metals, solubility of the, 16; cyanides of the, and their combinations with cyanide of potassium, 82, 92; on the structure of electro-precipitated, 300.
Metastyrole, 347.
Methyl, hyposulphate of, 364.
Microscope, on preserving salts for the, 71.
Middleton (J.) on fluorine in recent and fossil bones, and the sources from whence it is derived, 134.
Murray (R.) on the phænomena of sounds produced in a bar of soft iron, 201.
Muspratt (J. S.) on certain processes in which aniline is formed, 249; on toluidine, a new organic base, 367.
Napier (James) on the solubility of the metals in persulphate and perchloride of iron, 16; on the cyanides of the metals, and their combinations with cyanide of potassium: —Part I. Cyanide of gold, 82; Part II. Cyanide of silver, 92; on the decomposition of the double cyanides by an electric current, 158; on the decomposition of metallic salts by an electric current, 255.
Narcogenin, 173.
Narcotine, atomic weight of, 163; composition of, 163, 165; products of decomposition, 168, 177.
Nickel, solubility of, 20; discovery of pure oxide of, in the scum arising from smelting of copper, 384.
Nitraniline, 382.
Nitrates, 435; volumes occupied by certain, 440.
Nitric acid, action of, on chloraniline, 283; on styrole, 339; on metastyrole, 351.
Nitrobenzoic acid, 343.
Nitrometastyrole, 351.
Nitrostyrole, preparation of, 339.
Officers and Council, in 1844, 113; in 1845, 334.
Oils, essential, possessing no rotating energy, 45; hydrate of the, of laurel turpentine, 121; East Indian grass, 122.
Opianic acid, 172.
Ore, on brown iron, 321; composition and quantitative analysis, 322.
Oxide, on a class of double sulphates containing a magnesian, 49.
Oxides, decomposition of, by chlorine, 234.
Ozone, 395.
Parakomenic acid, 6.
Peas, analysis of the ash of, 193.
Percy (Dr. John) on a new hydrated phosphate of lime, 222.
Peruvian matico, on the pharmaceutical and chemical characters of the, 123.
Pharmacopœias, on the distilled waters of our, 261.
Phosphates, vegetable ashes rich in alkaline and earthy, 184; analysis of, 186; analysis of seed-ashes containing tribasic and bibasic, 195, 196; volumes occupied by, 418.
Phosphoric acid in vegetable ash, 189.
Plants, inorganic constituents of, 179; determination of the quantity of vegetable ash in, 190.
Platinum, products of decomposition of narcotine by bichloride of, 163, 168; bichloride of, and chloraniline, 280; bromaniline and bichloride of, 293.
Playfair (Lyon) on atomic volume and specific gravity, 401.
Potash, neutralization of various acids by hydrate of, 51; of hydrate of, by nitric and hydrochloric acids, 52; of hydrate of, by sulphuric acid, 58; of bichromate of, by hydrate of, 64; of acetic acid, by hydrate of, 65; of oxalic acid, *ib.*; binoxalate of, 66; quadroxalate of, 67; neutralization of bicarbonate of, with hydrate of, 68; of arsenic and phosphoric acids, by hydrate of, *ib.*; action of hydrate of, in fusion on isatin, 271; of fused, on chlorisatine, 272; on dichlorisatine, 285; on bromisatine, 289; on dibromisatine, 294; influence of solar rays on manganate of, 313.
Potassa in the Bonnington water, 209.
Potassium, on the cyanides of the metals, and their combination with

cyanide of, 82, 92; cyanide of gold and, 88; action of, on chloraniline, 285.
Precipitates, colour of, when exposed to solar rays, 316.
Precipitation, influence of the solar rays on, 312.
Pyrokomenic acid, 6.
Pyromeconate of copper, 3; of iron, 4.
Pyromeconic acid, 2, 5.
Pyromucic acid, 5.
Quadroxalate of potash, 67.
Report, Auditors', 112, 333.
Rhodomenia palmata, mannite contained in, 138.
Richardson (Thomas), analyses of farm-yard manure and of coal-gas, 309.
Rye, analysis of the ash of, 193.
Salts, on a means of preserving the crystals of, as permanent objects for microscopic investigation, 71; iron, from æthereal solution of meconic acid, 116; reduction of the, of peroxide of iron, by means of vegetable substances, 120; decomposition of, by chlorine, 234; decomposition of, of ammonia, 244; decomposition of metallic, by an electric current, 255; volumes occupied by certain, containing a large amount of hydrate water, 412; volume occupied by certain hydrated, rendered anhydrous, 433; ammoniacal, 460; volumes occupied by, 466; laws which regulate the volumes of, 476.
Sand, determination of the silica of the, in vegetable ash, 186.
Schweitzer (G.), on an analysis of the Bonnington water, near Leith, Scotland, 201.
Sea-weeds, occurrence of mannite in, 136.
Seed-ashes, analyses of, containing tribasic and bibasic phosphates, 195, 196, 197.
Silica, vegetable ashes rich in, 184, 186, 190.
Silver, curious change in the molecular structure of, 47; cyanide of, 92; komenate of, 120; new method of covering glass, by precipitation, with a coating of metallic, 128; on some of the substances which reduce oxide of, 242.
Smith (J. Denham) on ferric acid, 25; on the composition of some varieties of South American guano; with the description of a new mode of estimating ammonia, and of a process for separating lime from magnesia, when these earths exist in combination with phosphoric acid, 140.
Soda, on a class of double sulphates containing, 49; in the Bonnington water, 210; volumes occupied by carbonate of, 418.
Solar rays, influence of the, on precipitation, 312.
Solly (Edward) on a chemical lamp-furnace, 218.
Stenhouse (Dr. John) on the products of the distillation of meconic acid, 1; on some of the salts of meconic and komenic acid, 113; on the reduction of the salts of peroxide of iron by means of vegetable substances, 120; on the hydrate of the oil of laurel turpentine, 121; on East Indian grass oil, 122; on the occurrence of mannite in the *Laminaria saccharina* and other sea-weeds, 136; on a means of detecting kinic acid, 226; on some of the substances which reduce oxide of silver and precipitate it on glass in the form of a metallic mirror, 242.
Styrole, 334, 353; preparation of, 336; properties of, 337; composition of, 338; products of the decomposition of—action of nitric acid, 339; action of chromic acid on, 344; of fuming sulphuric acid on, 345; of bromine on, 345; of chlorine on, 346; of heat on, 347.
Subsalts, examination of, 460; volumes occupied by, 466.
Sulphates, on a class of double, containing soda and a magnesian oxide, 49; volumes of certain anhydrous and double, 422, 427.
Sulphuric acid in vegetable ash, 189.
Teas, green, of commerce, 73.
Tilley (Thomas) on the conversion of cane-sugar into a substance isomeric with cellulose and inulin, 384.
Tin, solubility of, 19.
Tobacco, analysis of the ashes of, 192.
Toluidine, 367; preparation of, 373; composition of, 375; properties of, *ib.*; compounds of, 377; sulphate of, 378; binoxalate of, *ib.*; hydrochlorate of, 379; platinchloride of,

ib.; products of the decomposition of, 380.
Toluol, preparation of, 371.
Tribromaniline, 296.
Trichloraniline, 286.
Triticum repens, or couch grass, supposed existence of mannite in the roots of, 139.
Turpentine, hydrate of the oil of laurel, 121.
Uric acid, on the chemical history of the products of the decomposition of, 9.
Vegetable substances, on the reduction of the salts of peroxide of iron by means of, 120.
Vegetables, inorganic compounds in the ashes of, 182.
Warington (Robert) on a curious change in the molecular structure of silver, 47; on a means of preserving the crystals of salts as permanent objects for microscopic investigation, 71; on the green teas of commerce, 73; on Mr. Drayton's new method of covering glass, by precipitation, with a coating of metallic silver, 128; on a curious change in the composition of bones taken from the guano, 223; on some commercial specimens of green glass, 247; on the distilled waters of our pharmacopœias, 261; on the action of animal charcoal, 326.
Water, Bonnington, analysis of the, 201; quantitative analysis of the soluble and earthy ingredients in, 206, 211; existence of phosphoric acid in the deep-well, of the London basin, 392; solubility of oxide of lead in pure, 399; volumes occupied by certain salts containing a large amount of hydrate, 412; sulphates with a small proportion of hydrate, 427.
Waters, on the distilled of our pharmacopœias, 261.
Way (John Thomas) on a spathic carbonate of iron, 105.
Wheat, analysis of the ash of, 193; on a specimen of diseased, 199.
Will (Dr. H.) on the inorganic constituents of plants, 179.
Williamson (Alexander W.) on the decomposition of oxides and salts by chlorine, 234; on ozone, 395.
Yorke (Lieut.-Col. P. I.) on brown iron ore, 321; on the solubility of oxide of lead in pure water, 399.

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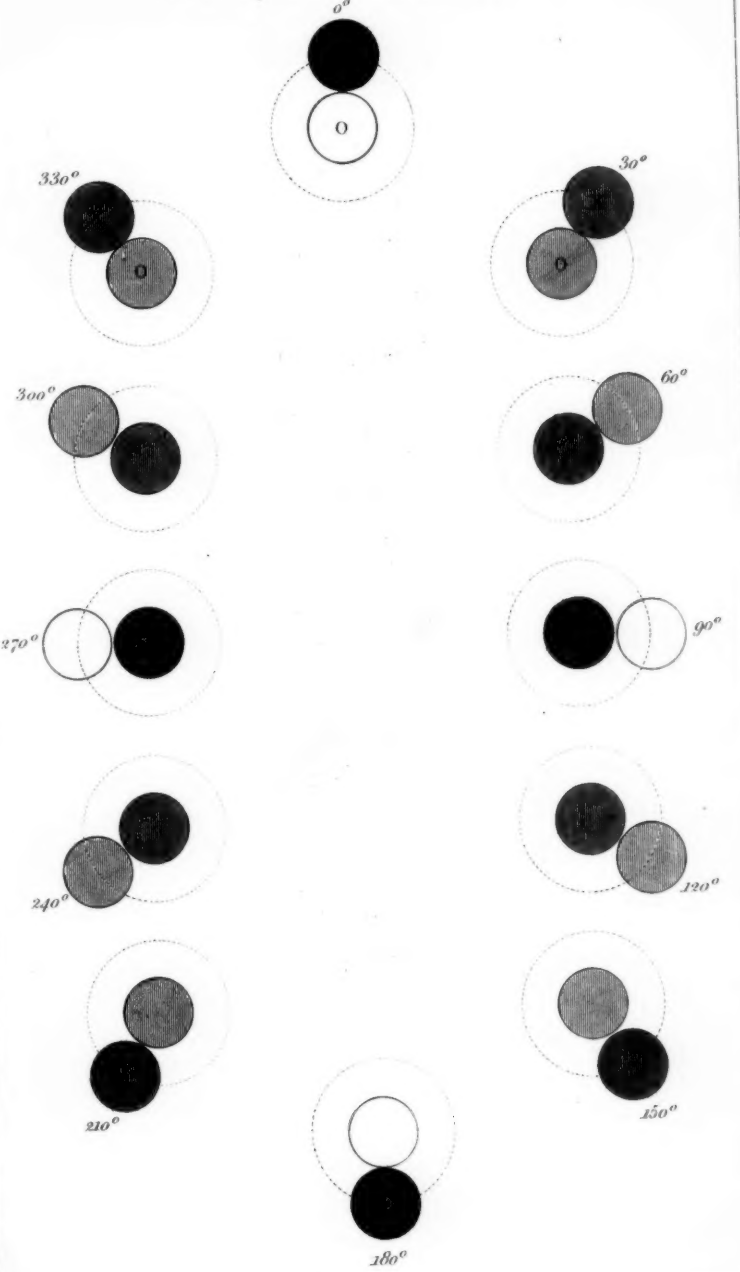

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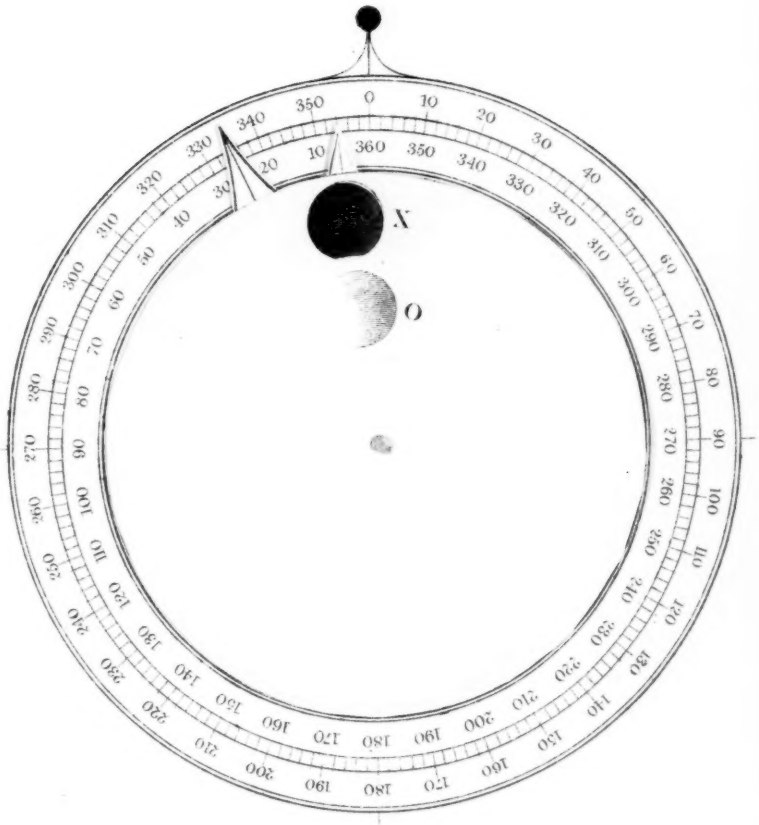

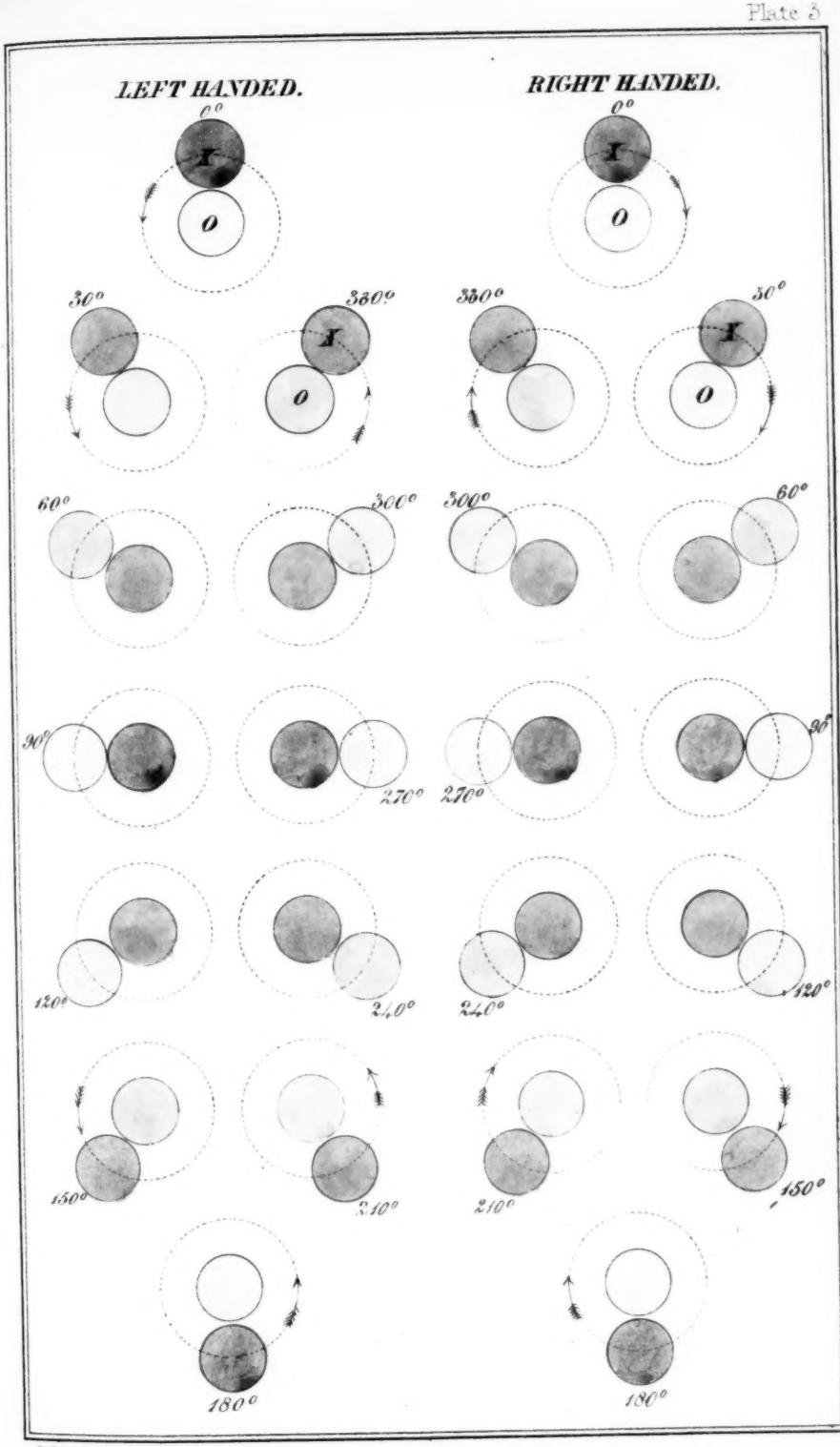

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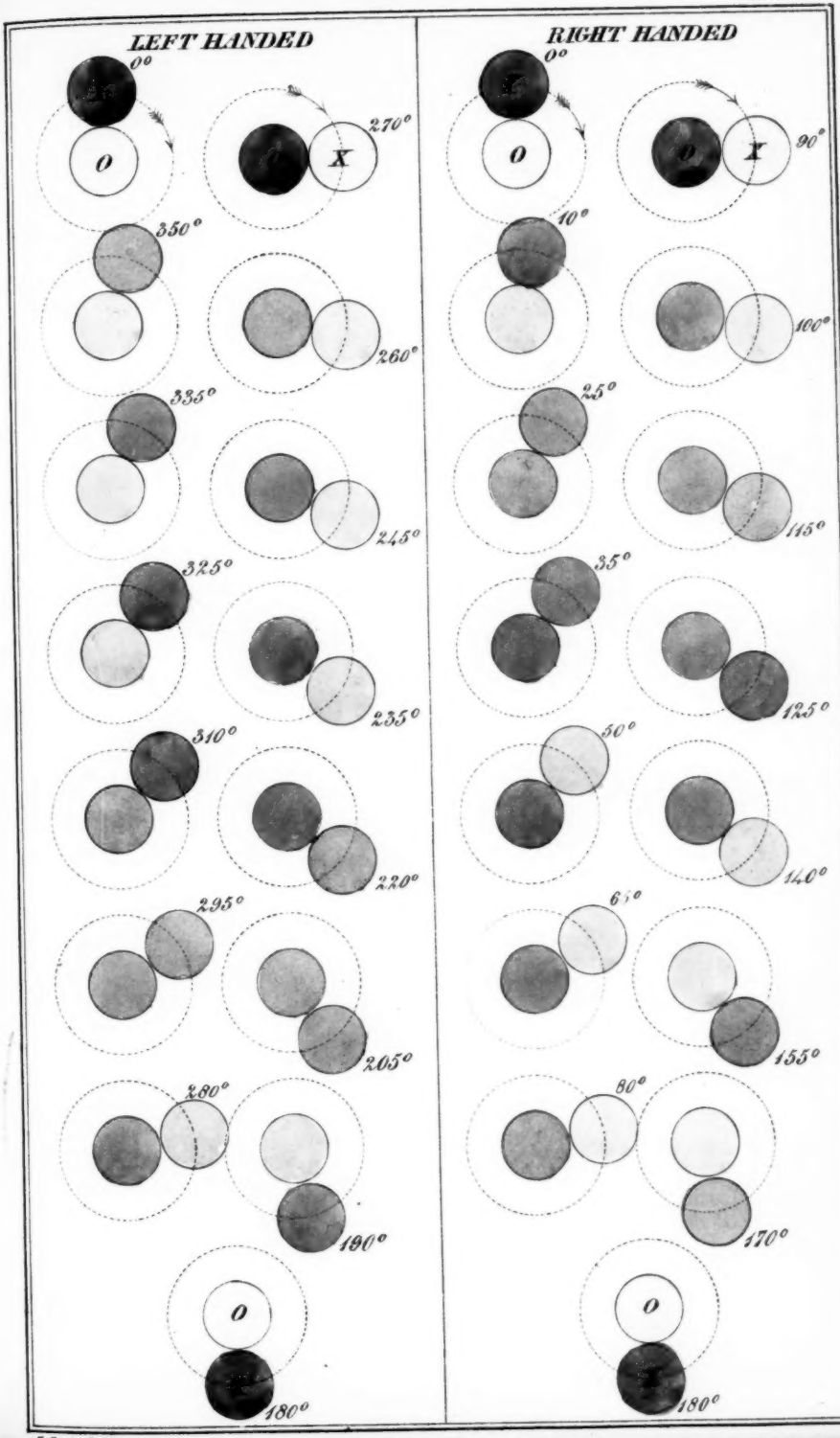

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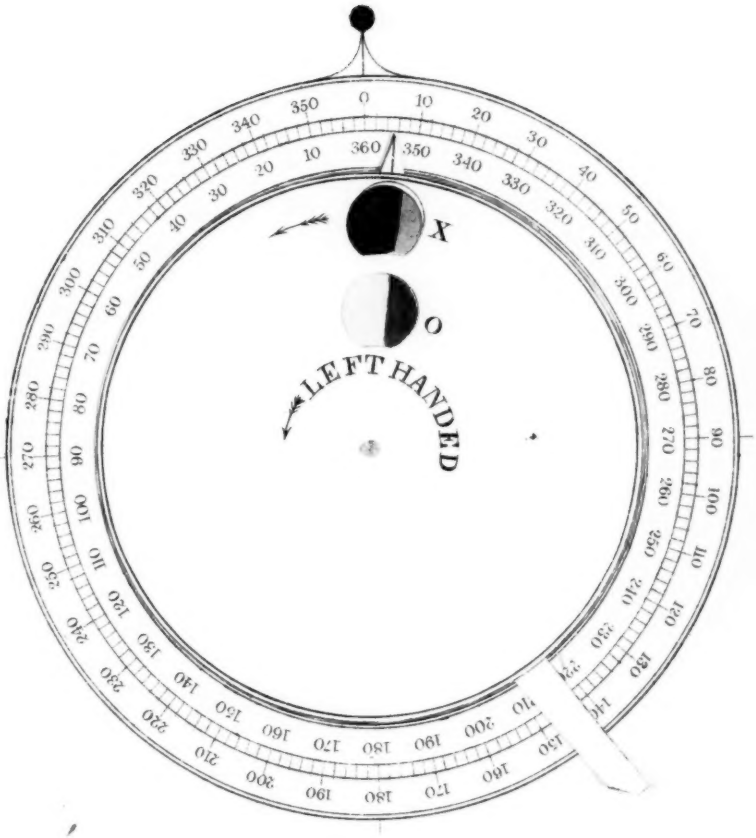

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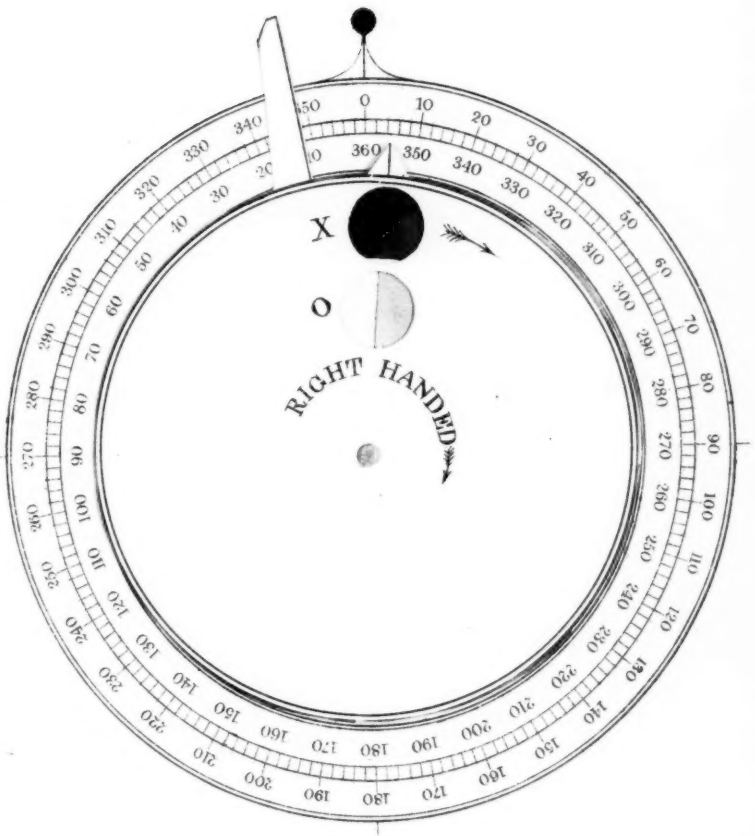
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